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$$\underset{\text{Bisulphide of carbon.}}{(C_2S_2)''S_2} + 2H_3N = \underset{\text{Sulphocarbamate of ammonium.}}{\left.\begin{matrix}[(C_2S_2)''H_2N]\\[H_4N]\end{matrix}\right\} S_2}$$

$$\underset{\text{Anhydrous Phtalic acid.}}{(C_{16}H_4O_4)''O_2} + 2H_3N = \underset{\text{Phtalamate of ammonium.}}{\left.\begin{matrix}[(C_{16}H_4O_4)''H_2N]\\[H_4N]\end{matrix}\right\} O_2}$$

$$\underset{\text{Anhydrous camphoric acid.}}{(C_{20}H_{14}O_4)''O_2} + 2H_3N = \underset{\text{Camphoramate of ammonium.}}{\left.\begin{matrix}[(C_{20}H_{14}O_4)''H_2N]\\[H_4N]\end{matrix}\right\} O_2}$$

The acid ethers of some dibasic acids when treated with ammonia also yield amidic acids.

$$\underset{\substack{\text{Methyl-salicylic acid}\\\text{Oil of Gaultheria}\\\text{procumbens}}}{\left.\begin{matrix}(C_{14}H_4O_2)''\\(C_2H_3)H\end{matrix}\right\} O_4} + 2H_3N = \underset{\text{Salicylamate of ammonium.}}{\left.\begin{matrix}[(C_{14}H_4O_2)''H_2N]\\[H_4N]\end{matrix}\right\} O_2} + \underset{\text{Methylic alcohol.}}{\left.\begin{matrix}C_2H_3\\H\end{matrix}\right\} O_2}$$

Amidic acids may also be conveniently produced by the action of water upon the secondary amides, containing a diatomic acid radical, which are often designated as imides. Instead of the imide, one of its metallic derivatives, may be employed. The reaction, which consists in the assimilation of 2 equivs. of water, is generally accomplished by boiling the amide with ammonia, and occasionally with carbonate of sodium.

$$\underset{\substack{\text{Succinyl-argenta-}\\\text{mide.}}}{\left.\begin{matrix}(C_8H_4O_4)''\\Ag\end{matrix}\right\} N} + H_2O_2 = \underset{\substack{\text{Succinamate of}\\\text{silver.}}}{\left.\begin{matrix}[(C_8H_4O_4)''H_2N]\\Ag\end{matrix}\right\} O_2}$$

By a similar fixation of 2 equivs. of water, many primary diamides are converted into the ammonium-compounds of secondary amidic acids. In this manner asparagin (malamide) is converted into aspartate (malamate) of ammonium:

$$\underset{\text{Asparagin.}}{\left.\begin{matrix}(C_8H_4O_6)''\\H_2\\H_2\end{matrix}\right\} N_2} + H_2O_2 = \underset{\text{Aspartate of ammonium.}}{\left.\begin{matrix}[(C_8H_4O_6)''H_2N]\\[H_4N]\end{matrix}\right\} O_2}$$

sebamide into sebamate of ammonium·—

$$\underbrace{\left.\begin{matrix}(C_{20}H_{16}O_4)''\\ H_2\\ H_2\end{matrix}\right\}N_2}_{\text{Sebamide.}} + H_2O_2 = \underbrace{\left.\begin{matrix}[(C_{20}H_{16}O_4)''H_2N]\\ [H_4N]\end{matrix}\right\}O_2}_{\text{Sebamate of ammonium.}}$$

Lastly, some peculiar reactions may be mentioned in which the ethers of the amidic acids are formed.

Chlorocarbonate of ethyl, when treated with ammonia, yields carbamate of ethyl, generally called *urethane*.

$$\underbrace{\left.\begin{matrix}(C_2O_2)''\\ C_4H_5\end{matrix}\right\}\begin{matrix}O_2\\ Cl\end{matrix}}_{\text{Chlorocarbonate of ethyl.}} + 2H_3N = \underbrace{\left.\begin{matrix}[(C_2O_2)''H_2N]\\ C_4H_5\end{matrix}\right\}O_2}_{\text{Carbamate of ethyl.}} + [H_4N]Cl$$

Oxalate of ethyl gives, with a small quantity of alcoholic ammonia, oxamate of ethyl (oxamethane).

$$\underbrace{\left.\begin{matrix}(C_4O_4)''\\ (C_4H_5)_2\end{matrix}\right\}O_4}_{\text{Oxalic ether.}} + H_3N = \underbrace{\left.\begin{matrix}[(C_4O_4)''H_2N]\\ C_4H_5\end{matrix}\right\}O_2}_{\text{Oxamate of ethyl.}} + \underbrace{\left.\begin{matrix}C_4H_5\\ H\end{matrix}\right\}O_2}_{\text{Alcohol.}}$$

It is very probable that Chemists will ultimately recognize as true amidic acids a number of compounds, the constitution of which is still under discussion. In a previous section of this paper, we have enumerated a series of remarkable bodies, which hold an intermediate position between acids and bases. Glycocine and alanine, benzamic and anisamic acids have been viewed as primary monamines, as ammonia, in which 1 eq. of hydrogen is replaced by monatomic molecules; but they may be equally well considered as amidic acids, if we assume in them the existence of diatomic radicals.

Glycocine (Acetamic acid, glycolylamic acid)

$$C_4H_5NO_4 = \left.\begin{matrix}C_4H_3O_4\\ H\\ H\end{matrix}\right\}N = \left.\begin{matrix}[(C_4H_2O_2)''H_2N]\\ H\end{matrix}\right\}O_2$$

Alanine (Propionamic acid, lactylamic acid)

$$C_6H_7NO_4 = \left.\begin{matrix}C_6H_5O_4\\ H\\ H\end{matrix}\right\}N = \left.\begin{matrix}[(C_6H_4O_2)''H_2N]\\ H\end{matrix}\right\}O_2$$

Benzamic acid $C_{14}H_7NO_4 = \left.\begin{matrix}C_{14}H_5O_4\\H\\H\end{matrix}\right\}N$

$= \left.\begin{matrix}[(C_{14}H_4O_2)''H_2N]\\H\end{matrix}\right\}O_2$

Anisamic acid $C_{16}H_9NO_6 = \left.\begin{matrix}C_{16}H_7O_6\\H\\H\end{matrix}\right\}N$

$= \left.\begin{matrix}[(C_{16}H_6O_4)''H_2N]\\H\end{matrix}\right\}O_2$

The view, which claims these substances as amidic acids, is supported by many important facts. All these bodies contain 1 molecule of hydrogen, in a remarkably mobile condition, readily replaceable by metals, and readily re-assumable, much more so than in undoubtedly established monamines and monamides. Their formation is likewise in favour of this view; chloracetic acid and nitrobenzoic acid, which are respectively convertible into glycocine and benzamic acid, obviously still retain the original construction of acetic and benzoic acids. Considered as amidic acids, glycocine and benzamic acids are likewise constructed upon the water-type.

Acetic acid $\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}O_2$

Chloracetic acid $\left.\begin{matrix}C_4(H_2Cl)O_2\\H\end{matrix}\right\}O_2$

Acetamic $\left.\begin{matrix}C_4(H_2,H_2N)O_2\\H\end{matrix}\right\}O_2$ or

Glycolylamic acid $\left.\begin{matrix}[(C_4H_2O_2)''H_2N]\\H\end{matrix}\right\}O_2$

Benzoic acid $\left.\begin{matrix}C_{14}H_5O_2\\H\end{matrix}\right\}O_2$

Nitrobenzoic acid $\left.\begin{matrix}C_{14}(H_4,NO_4)O_2\\H\end{matrix}\right\}O_2$

Amidobenzoic $\left.\begin{matrix}C_{14}(H_4,H_2N)O_2\\H\end{matrix}\right\}O_2$ or

Benzamic acid $\left.\begin{matrix}[(C_{14}H_4O_2)''H_2N]\\H\end{matrix}\right\}O_2$

The transformation, if I may say so, is accomplished on the left-hand side of the water-bracket.

At the conclusion of this paper some remarkable derivatives of these bodies, of very recent date, will be noticed, which are perfectly unintelligible, unless we view the mother compounds as amidic acids.

The formation of these substances has been mentioned in the chapter on the formation of the organic bases.

Tertiary Monamidic Acids.

a. Substitution of 1 monatomic and 1 diatomatic acid-radical.

Salicyl-benzamic acid $C_{28}H_{11}NO_6 = \left.\begin{matrix}[(C_{14}H_4O_2)''(C_{14}H_5O_2)HN] \\ H\end{matrix}\right\} O_2$

Salicyl-cumyl-amic acid $C_{34}H_{17}NO_6 = \left.\begin{matrix}[(C_{14}H_4O_2)''(C_{20}H_{11}O_2)HN] \\ H\end{matrix}\right\} O_2$

b. Substitution of 1 diatomic acid-radical and 1 monatomic alcohol-radical.

Phenyl-carbamic acid (Anthranilic acid) $C_{14}H_7NO_4 = \left.\begin{matrix}[(C_2O_2)''(C_{12}H_5)HN] \\ H\end{matrix}\right\} O_2$

Amyl-sulphocar-bamic acid $C_{12}H_{13}NS_4 = \left.\begin{matrix}[(C_2S_2)''(C_{10}H_{11})HN] \\ H\end{matrix}\right\} S_2$

Phenyl-sulphamic acid (Sulphanilic acid) $C_{12}H_7NO_6S_2 = \left.\begin{matrix}[(S_2O_4)''(C_{12}H_5)HN] \\ H\end{matrix}\right\} O_2$

Ethyl-oxamic acid $C_8H_7NO_6 = \left.\begin{matrix}[(C_4O_4)''(C_4H_5)HN] \\ H\end{matrix}\right\} O_2$

Phenyl-succinamic acid (Succinanilic acid) $C_{20}H_{11}NO_6 = \left.\begin{matrix}[(C_8H_4O_4)''(C_{12}H_5)HN] \\ H\end{matrix}\right\} O_2$

Phenyl-itaconamic acid (Itaconanilic acid) $C_{22}H_{11}NO_6 = \left.\begin{matrix}[(C_{10}H_4O_4)''(C_{12}H_5)HN] \\ H\end{matrix}\right\} O_2$

Dinitrophenyl-ci-traconamic acid $C_{22}H_9N_3O_{14} = \left.\begin{matrix}[(C_{10}H_4O_4)'' \\ (C_{12}[H_3(NO_4)_2])HN] \\ H\end{matrix}\right\} O_2$

Phenylcamphoramic acid (Camphoranilic acid) $C_{32}H_{21}NO_6 = \left.\begin{matrix}[(C_{20}H_{14}O_4)''(C_{12}H_5)HN] \\ H\end{matrix}\right\} O_2$

Phenyl-phtalamic acid (Phtalanilic acid) $C_{28}H_{11}NO_6 = \left.\begin{matrix}[(C_{16}H_4O_4)''(C_{12}H_5)HN] \\ H\end{matrix}\right\} O_2$

Phenyl-malamic acid (Malanilic acid) $C_{20}H_{11}NO_8 = \left.\begin{matrix}[(C_8H_4O_6)''(C_{12}H_5)HN] \\ H\end{matrix}\right\} O_2$

If glycocine be viewed as a secondary amidic acid, as glycolylamic acid, hippuric acid becomes a tertiary amidic acid.

Hippuric acid (Glycolyl-benzamic acid) $C_{18}H_9NO_6$ $\left.\begin{matrix}C_4H_3O_4 \\ C_{14}H_5O_2 \\ H\end{matrix}\right\} N = \left.\begin{matrix}\left[\begin{matrix}(C_4H_2O_2)'' \\ (C_{14}H_5O_2)\end{matrix}\right]HN \\ H\end{matrix}\right\} O_2$

The tertiary amidic acids, which contain 2 acid molecules, are simply obtained by the action of monatomic chlorides upon secondary amidic acids.

$\left.\begin{matrix}[(C_{14}H_4O_2)''H_2N] \\ H\end{matrix}\right\} O_2 + (C_{14}H_5O_2)Cl =$

Salicylamic acid. Chloride of benzoyl.

$$HCl + \left.\begin{matrix}\left[\begin{matrix}(C_{14}H_4O_2)'' \\ (C_{14}H_5O_2)\end{matrix}\right]HN \\ H\end{matrix}\right\} O_2$$

Salicyl-benzamic acid.

The tertiary acids containing 1 diatomic acid-molecule and 1 monatomic alcohol-molecule, are formed by submitting monamines to those processes which, when applied to ammonia, give rise to the formation of secondary amidic acids.

Action of heat on the acid salts of primary monamines with diatomic acids.

$\left.\begin{matrix}(C_4O_4)'' \\ [(C_4H_5)H_3N]H\end{matrix}\right\} O_4 = H_2O_2 + \left.\begin{matrix}[(C_4O_4)''(C_4H_5)HN] \\ H\end{matrix}\right\} O_2$

Acid oxalate of ethylamine. Ethyl-oxamic acid.

$$\underbrace{\left.\begin{matrix}(S_2O_4)''\\ [(C_{12}H_5)H_3N]H\end{matrix}\right\}O_4}_{\text{Acid sulphate of phenylamine.}} = H_2O_2 + \underbrace{\left.\begin{matrix}[(S_2O_4)''(C_{12}H_5)HN]\\ H\end{matrix}\right\}O_2}_{\text{Phenyl-sulphamic acid.}}$$

$$\underbrace{\left.\begin{matrix}(C_{10}H_4O_4)''\\ [(C_{12}H_5)H_3N]H\end{matrix}\right\}O_4}_{\text{Acid itaconate of phenylamine.}} = H_2O_2 + \underbrace{\left.\begin{matrix}[(C_{10}H_4O_4)''(C_{12}H_5)HN]\\ H\end{matrix}\right\}O_2}_{\text{Phenyl-itaconamic acid.}}$$

Action of the anhydrides of dibasic acids upon the primary monamines.

$$\underbrace{2\left[\left.\begin{matrix}C_{10}H_{11}\\ H\\ H\end{matrix}\right\}N\right]}_{\text{Amylamine.}} + (C_2S_2)''S_2 = \underbrace{\left.\begin{matrix}[(C_2S_2)''(C_{10}H_{11})HN]\\ [(C_{10}H_{11})H_3N]\end{matrix}\right\}S_2}_{\text{Amyl-sulphocarbamate of amylamine.}}$$

$$\underbrace{2\left[\left.\begin{matrix}C_{12}H_5\\ H\\ H\end{matrix}\right\}N\right]}_{\text{Phenylamine.}} + \underbrace{(C_{20}H_{14}O_4)''O_2}_{\text{Camphoric anhydride.}} = \underbrace{\left.\begin{matrix}[(C_{20}H_{14}O_4)''(C_{12}H_5)HN]\\ [(C_{12}H_5)H_3N]\end{matrix}\right\}O_2}_{\text{Phenyl-camphoramate of phenylamine.}}$$

Action of water upon tertiary monamides, containing a diatomic acid-radical and a monatomic alcohol-radical.

The largest number of tertiary amidic acids has been procured by this process, which is conveniently accomplished by ebullition with ammonia.

$$\underbrace{\left.\begin{matrix}(C_8H_4O_4)''\\ (C_{12}H_5)\end{matrix}\right\}N}_{\text{Phenyl-succinimide.}} + H_2O_2 = \underbrace{\left.\begin{matrix}[(C_8H_4O_4)''(C_{12}H_5)HN]\\ H\end{matrix}\right\}O_2}_{\text{Phenyl-succinamic acid.}}$$

$$\underbrace{\left.\begin{matrix}(C_{16}H_4O_4)''\\ (C_{12}H_5)\end{matrix}\right\}N}_{\text{Phenyl-phtalimide.}} + H_2O_2 = \underbrace{\left.\begin{matrix}(C_{16}H_4O_4)''(C_{12}H_5)HN]\\ H\end{matrix}\right\}O_2}_{\text{Phenyl-phtalamic acid.}}$$

Some of the tertiary monamidic acids have been obtained in reactions, which are as yet isolated. Phenyl-carbamic (anthranilic) acid is formed by the action of hydrate of potassa upon indigo.

$$\underbrace{C_{16}H_5NO_2}_{\text{Indigo.}} + 2(KO,HO) + 2H_2O_2 = K_2C_2O_6 + 4H + \underbrace{C_{14}H_7NO_4}_{\text{Anthranilic acid.}}$$

Quartary Monamidic Acids.

The only terms of this class which are at present known are the following:—

Phenyl-citramic acid $C_{24}H_{11}NO_{10} = \left.\begin{matrix}[(C_{12}H_5O_8)'''(C_{12}H_5)N] \\ H\end{matrix}\right\} O_2$

Phenyl-aconitamic acid $C_{24}H_9NO_8 = \left.\begin{matrix}[(C_{12}H_3O_6)'''(C_{12}H_5)N] \\ H\end{matrix}\right\} O_2$

The former of these compounds is produced by the action of heat upon the citrate of phenylamine, containing 1 equiv. of the base.

$$\underbrace{\left.\begin{matrix}(C_{12}H_5O_8)''' \\ [(C_{12}H_5)H_3N]H_2\end{matrix}\right\} O_6}_{\text{Citrate of phenylamine.}} = 2H_2O_2 + \underbrace{\left.\begin{matrix}[C_{12}H_5O_8)'''(C_{12}H_5)N] \\ H\end{matrix}\right\} O_2}_{\text{Phenyl-citramic acid.}}$$

The second is obtained in a remarkable process. The action of pentachloride of phosphorus upon phenyl-citramic acid gives rise to the formation of a very interesting chloride, corresponding, on the electro-negative side of the series, to chloride of ammonium, as chloride of tetrethylammonium does, on the electro-positive side.

$$\underbrace{\left.\begin{matrix}[(C_{12}H_5O_8)'''(C_{12}H_5)N] \\ H\end{matrix}\right\} O_2}_{\text{Phenyl-citramic acid.}} + 2PCl_5 = 2[(PO_2)'''Cl_3] + 3HCl + \underbrace{[(C_{12}H_3O_6)'''(C_{12}H_5)N]Cl}_{\text{Chloride of phenyl-aconityl-ammonium.}}$$

The chloride of phenyl-aconityl-ammonium, when coming in contact with water, splits into hydrochloric and phenyl-aconitamic acid.

$$\underbrace{[(C_{12}H_3O_6)'''(C_{12}H_5)N]Cl}_{\text{Chloride of phenyl-aconityl-ammonium.}} + H_2O_2 = HCl + \underbrace{\left.\begin{matrix}[(C_{12}H_3O_6)'''(C_{12}H_5)N] \\ H\end{matrix}\right\} O_2}_{\text{Phenyl-aconitamic acid.}}$$

Diamine-Amidic Acids.

In tracing the history of the basic derivatives of ammonia, we were led to the assumption that compound monatomic metals similar to ammonium, may be formed by the association of 1 equiv. of hydrogen, not only with 1 molecule of ammonia, but with 2, and perhaps with 3 molecules of ammonia. We arrived in this manner at compounds of monamine-ammonium, diamine-ammonium and triamine-ammonium, and we quoted several substances which appear to be constructed upon this type, one of the most conspicuous members of the group being, perhaps, the—

Hydrated oxide of methyl-diethylene-diphenyl-diamine-ammonium $[(C_2H_3)\left((C_4H_4)''_2(C_{12}H_5)_2\underset{H}{N_2}\right)]\Big\}O_2$.

Some similarly constructed compounds appear to exist among the acid derivatives of ammonia. Their number is as yet very limited.

Oxalyl-nitrophenylene-diamine-amidic acid (Nitrazophenyl-oxamic acid) $= [H\left((C_4O_4)''(C_{12}[H_3,NO_4])''\underset{H}{H_2N_2}\right)]\Big\}O_2$

Citraconyl-nitrophenylene-diamine-amidic acid (Nitrazophenyl-citraconamic acid) $= [H\left((C_{10}H_4O_4)''(C_{12}[H_3,NO_4])''\underset{H}{H_2N_2}\right)]\Big\}O_2$

Diphenyl-citryl-diamine-amidic acid (Citrobianilic acid) $= [H\left((C_{12}H_5O_8)'''(C_{12}H_5)_2\underset{H}{HN_2}\right)]\Big\}O_2$

The two former of these compounds are produced by the action of heat upon the acid azophenylamine-salts of oxalic and citraconic acids with elimination of water.

$$\frac{[H\left((C_{12}[H_3,NO_4])''H_4N_2\right)]H\Big\}O_4}{\text{Acid oxalate of azophenylamine.}}$$

$$= H_2O_2 + \underbrace{\left.\begin{matrix}[H\left((C_4O_4)''(C_{12}[H_3,NO_4])''H_2N_2\right)]\\ H\end{matrix}\right\} O_2}_{\text{Nitrazophenyloxamic acid.}}$$

Citrobianilic acid is formed by heating phenyl-citramide with ammonia to a temperature of 165° C., when 2 equivs. of water are fixed and 1 equiv. of phenylamine separates.

$$\underbrace{\left.\begin{matrix}(C_{12}H_5O_8)'''\\ (C_{12}H_5)_3\\ H_3\end{matrix}\right\} N_3 + H_2O_2}_{\text{Triphenyl-citryl-triamide.}}$$

$$= \underbrace{\left.\begin{matrix}[H\left((C_{12}H_5O_8)'''(C_{12}H_5)_2HN_2\right)]\\ H\end{matrix}\right\} O_2}_{\text{Diphenyl-citryl-diamine-amidic acid.}} + \underbrace{\left.\begin{matrix}C_{12}H_5\\ H\\ H\end{matrix}\right\} N}_{\text{Phenylamine.}}$$

Diamidic Acids.

These remarkable compounds have been only recently discovered;* their study is not yet completed. The diamidic acids correspond to 2 molecules of water, and represent among the acid derivatives of ammonia, the hydrated dioxides of diammonium among the bases.

If we represent by the terms benzoylene and anisylene, two diatomic molecules $C_{14}H_4O_2$ and $C_{16}H_6O_4$, which we conceive to be generated respectively from benzoyl $C_{14}H_5O_2$, and anisyl $C_{16}H_7O_4$, by the elimination of 1 equiv. of hydrogen, the diamidic acids to which we allude, may be thus represented:

Nitryl-dibenzoylene-diamic acid $C_{28}H_{11}N_3O_8 = \left.\begin{matrix}[(N)'''(C_{14}H_4O_2)_2''HN_2]''\\ H_2\end{matrix}\right\} O_4$

Nitryl-dianisylene-diamic acid $C_{32}H_{15}N_3O_{12} = \left.\begin{matrix}[(N)'''(C_{16}H_6O_4)_2''HN_2]''\\ H_2\end{matrix}\right\} O_4$

The formation of these acids is exceedingly interesting. They are obtained by submitting alcoholic solutions of benzamic and anisamic acids (secondary monamidic acids) to the action of nitrous acid, when 3 equivs. of hydrogen are eliminated, from 2 equivs. of these acids, by the oxygen of the nitrous acid, whose nitrogen enters into the new system, linking together by

* P. Griess, Unpublished Researches.

its triatomic substitution-power, 2 molecules of the original compounds.

$$2\left[\left[(C_{14}H_4O_2)''\begin{matrix}H\\H\end{matrix}N\right]\right\}O_2\Big] + NO_3 = 3HO$$

Benzamic acid.

$$+ \left[(N)'''(C_{14}H_4O_2)_2''\begin{matrix}H_2\end{matrix}N_2\right]''\Big\}O_4$$

Nitryl-dibenzoylene-diamic acid.

$$2\left[\left[(C_{16}H_6O_4)''\begin{matrix}H\\H\end{matrix}N\right]\right\}O_2\Big] + NO_3 = 3HO$$

Anisamic acid.

$$+ \left[(N)'''(C_{16}H_6O_4)_2''\begin{matrix}H_2\end{matrix}N_2\right]''\Big\}O_4$$

Nitryl-dianisylene-diamic acid.

Triamidic acids have not yet been obtained. They will probably be produced by the action of nitrous acid upon the alcoholic solutions of tertiary monamidic acids. Hippuric acid thus treated might possibly be converted into a tribasic acid of the formula:—

$$\left[(N)'''(C_4H_2O_2)_3''(C_{14}H_5O_2)_3\right]'''\Big\}O_6$$

$$H_3$$

In the preceding paragraphs I have endeavoured to give an outline of the chemical history of the type Ammonia, such as it exhibits itself at the present moment. No department of Chemistry, perhaps, reflects in a more salient manner the rapid progress of science during the last quarter of a century. Nearly all the bodies mentioned in this paper were discovered during that period; nine-tenths, in fact, the very compounds which have most assisted in the elaboration of our theoretical views, are the fruits of the last ten years.

Though much has been achieved, more is left to be done. But even now, while so many known substances remain to be finally grouped and classified, and while countless groups and classes remain

to be discovered, yet the general features of the system are distinctly perceptible, and the time is rapidly approaching when, losing sight of the chaotic mass of overwhelming detail, the eye may rest with complacency upon the simple beauty of the law which governs the construction of the bodies belonging to the type of ammonia.

In conclusion I append a table embodying in a synoptical form the principal groups of ammonia-derivatives enumerated in the preceding pages.

TYPE AMMONIA.

$$\left.\begin{matrix} H \\ H \\ H \end{matrix}\right\} N$$

Positive Series. Substitution of Basic Radicals.		*Negative Series.* Substitution of Acid Radicals.
AMINES.		AMIDES.
Monamines.		*Monamides.*
Primary monamines	$\left.\begin{matrix} A \\ H \\ H \end{matrix}\right\} N$	Primary monamides
Secondary monamines	$\left.\begin{matrix} A \\ B \\ H \end{matrix}\right\} N$	Secondary monamides
Tertiary monamines	$\left.\begin{matrix} A \\ B \\ C \end{matrix}\right\} N$	Tertiary monamides

TYPE DIAMMONIA.

$$\left.\begin{matrix} H_2 \\ H_2 \\ H_2 \end{matrix}\right\} N_2$$

Diamines.		*Diamides.*
Primary diamines	$\left.\begin{matrix} A_2 \\ H_2 \\ H_2 \end{matrix}\right\} N_2$	Primary diamides
Secondary diamines	$\left.\begin{matrix} A_2 \\ B_2 \\ H_2 \end{matrix}\right\} N$	Secondary diamides
Tertiary diamines	$\left.\begin{matrix} A_2 \\ B_2 \\ C_2 \end{matrix}\right\} N$	Tertiary diamides

TYPE TRIAMMONIA.

$$\left.\begin{matrix} H_3 \\ H_3 \\ H_3 \end{matrix}\right\} N_3$$

Triamines.		*Triamides.*
Primary triamines	$\left.\begin{matrix} A_3 \\ H_3 \\ H_3 \end{matrix}\right\} N_3$	Primary triamides
	$\left.\begin{matrix} A_3 \\ B_3 \\ H_3 \end{matrix}\right\} N_3$	Secondary triamides
Tertiary triamines	$\left.\begin{matrix} A_3 \\ B_3 \\ C_3 \end{matrix}\right\} N_3$	Tertiary triamides

TYPE TETRAMMONIA.

$$\left.\begin{matrix} H_4 \\ H_4 \\ H_4 \end{matrix}\right\} N_4$$

Tetramines.		*Tetramides.*
	.....	
Tertiary tetramines	$\left.\begin{matrix} A_4 \\ B_4 \\ C_4 \end{matrix}\right\} N_4$	

TYPE HYDRATED OXIDE OF AMMONIUM (Water).

$$\left.\begin{matrix} [H_4N] \\ H \end{matrix}\right\} O_2$$

Monammonium-Bases.		*Monamidic Acids.*
Primary monammonium-bases (Metalammonium-bases.)	$\left.\begin{matrix} [AH_3N] \\ H \end{matrix}\right\} O_2$	
	$\left.\begin{matrix} [ABH_2N] \\ H \end{matrix}\right\} O_2$	Secondary monamidic acids.
	$\left.\begin{matrix} [ABCHN] \\ H \end{matrix}\right\} O_2$	Tertiary monamidic acids.
Quartary monammonium-bases	$\left.\begin{matrix} [ABCDN] \\ H \end{matrix}\right\} O_2$	Quartary monamidic acids.

TYPE HYDRATED OXIDE OF DIAMINE-AMMONIUM.

$$\left.\begin{matrix}[H(H_3N)_2] \\ H\end{matrix}\right\} O_2$$

Diamine-Ammonium-Bases.		*Diamine-Amidic Acids.*
Primary diamine-ammonium-bases (Metal-ammonium-bases)	$\left.\begin{matrix}[H(AH_2N)_2] \\ H\end{matrix}\right\} O_2$	
	$\left.\begin{matrix}[H(ABHN)_2] \\ H\end{matrix}\right\} O_2$	Secondary diamine-amidic acids.
	$\left.\begin{matrix}[H(ABCN)_2] \\ H\end{matrix}\right\} O_2$	Tertiary diamine-amidic acids.
Quartary diamine-ammonium-bases.	$\left.\begin{matrix}[A(BCDN)_2] \\ H\end{matrix}\right\} O_2$	

TYPE HYDRATED DIOXIDE OF DIAMMONIUM.

$$\left.\begin{matrix}[H_8N_2]'' \\ H_2\end{matrix}\right\} O_4$$

Diammonium-Bases.		*Diamidic Acids.*
.....		
Quartary diammonium-bases	$\left.\begin{matrix}[A_2B_2C_2D_2N_2]'' \\ H_2\end{matrix}\right\} O_4$	Quartary diamidic acids.

XIII.—*On some Derivatives from the Olefines.*

BY FREDERICK GUTHRIE, Ph.D.

First Memoir.

THOSE hydrocarbons which consist of equal numbers of equivalents of hydrogen and carbon (H = 1, C = 6) of which ethylene is the historical prototype, have of late received a large share of the attention of chemists. During the first quarter of the present century, the separation of ethylene from ethylic alcohol by substances which have strong affinity for water, was accepted by many as evidence of this body being the true radical of alcohol. The possibility of the synthesis of alcohol from the same hydrocarbon,

which was early indicated, and which has of late received complete corroboration, naturally supports the same view.

The isolation of the so-called organic radicals, the hydrides of the olefines, and more especially the *manner* of their isolation, has so far substantiated their claim to being viewed as radicals in the earlier restricted sense of the word; but the idea conveyed by the term radical has, meanwhile, undergone a wide extension.

In order to define the sense in which I employ this term, it may be remarked that between a compound body and its ultimate elements there exist certain possible derivatives of an inferior "order," each of which, as well as the ultimate elements themselves has strictly an equal claim to be considered as a radical of the body. The number of such derivatives depends of course upon the complexity or, *cæteris paribus*, upon the equivalent of the original substance.

Thus from ethylic alcohol we may obtain aldehyde, hydride of ethyl, ethyl, ethylene, hydride of methyl, carbonic acid, water and others; each of which is a *proximate* radical, in distinction to carbon, hydrogen, and oxygen, which are *ultimate* radicals or elements.

In this sense a radical is nothing more than a proximate element or molecule: and the continual reappearance of one and the same such molecule is to be taken, less as proof of an innate combining effort of its parts, than as evidence of uniformity in the physical influences to which it is subjected. The arrangement of the constituents of a substance, and the expression thereof by a formula can only be considered absolute as long as such influences remain invariable. But when the latter are so changed as so affect a recomposition of the elements in a different order, then the rational formula must recognize such rearrangement and vary in accordance with the forces which effect it. When, therefore, one body determines the splitting of a complex second body into certain molecules, such molecules are the radicals of the second body *relatively* to the first, and to the physical conditions accompanying the change.

Partly on account of the olefines being in this sense radicals of their alcohols, partly on account of their belonging to the class of so called diatomic bodies, whose discussion has thrown much light on organic chemistry, I have thought them deserving of special study.

Ethylene has the property of combining directly with two equivalents of chlorine, bromine and iodine, forming therewith the well known compounds $C_4H_4Cl_2$, $C_4H_4Br_2$, $C_4H_4I_2$, for our

knowledge of which we are indebted to Deimann and his associates, to Balard and to Faraday respectively. Löwig has moreover shown that the corresponding sulphur-compound $C_4H_4S_2$ may be obtained by the action of protosulphide of potassium upon the first of these bodies. Although many derivatives have been obtained from these substances, both by the substitution of the halogens for hydrogen, and by the elimination of the hydracids by alkaline oxides, their history is still very incomplete: firstly, inasmuch as the analogy between the ethylene compounds and those of the higher olefines is very imperfect; and further, because few successful attempts have been made to determine the character of the diatomic haloid-molecule, in the sense of ascertaining if, and when, one or both of its atoms may be replaced by similar ones, or by molecules functioning as such.

A description of some experiments performed in this direction furnishes the matter of the present memoir.

In selecting suitable olefines, ethylene and amylene appeared to offer the greatest promise of interesting results: partly because they can both be obtained in a state of great purity, partly because, being somewhat widely separated upon the olefine series, analogous derivatives or reactions common to both would point to similar ones in the two intermediate terms, propylene and butylene; while the nature of their dissimilarities would also to some extent indicate the nature of the derivatives from the same two bodies and their behaviour under similar conditions.

My first object was to combine these two olefines with some of the combinations of the halogens which are known to exist, and some of which are exhibited in the following table:—

Cl_2					
ClBr	Br_2				
ClI	BrI	I_2			
ClO	BrO	IO	O_2		
ClCy	BrCy	ICy	OCy	Cy_2	
ClS	BrS	IS	OS	CyS	S_2
ClS_2					

Although some of these bodies have not yet been obtained, and the definite nature of the composition of others is still doubtful, yet there can be little question as to the possibility of the existence of all. As, however, the members of the first or chlorine column have been most fully studied, and as chlorine itself shows pre-

eminently the power of combining with the olefines, the behaviour of these chlorides towards ethylene and amylene was the first subject of investigation.

Action of the Chlorides of Sulphur upon Ethylene and Amylene.

I shall call the body ClS_2, the bisulphide of chlorine, and the body ClS or Cl_2S_2 the chloride of sulphur; it will be seen in the sequel that this nomenclature avoids the introduction of an ambiguity in speaking of the derivatives of the two compounds.

Action of bisulphide of chlorine upon amylene.—Into a flask containing 52 grms. of bisulphide of chlorine, pure and dry amylene was allowed to drop slowly, the flask being kept cold by agitation in water. Immediate combination, accompanied by the liberation of heat, ensued, no permanent gas being evolved. The amylene was added until no further evolution of heat occurred on the addition of fresh quantities. The flask containing the product so obtained was then heated for several hours in a water-bath at 100°C. A distillate was thereby obtained, which consisted entirely of the excess of amylene only contaminated by a slight trace of hydrochloric acid. The residue in the flask, which had deepened somewhat in colour, weighed 104 grms. The bisulphide of chlorine had therefore combined with exactly its own weight of amylene, that is, 52 grms. In another experiment 51 grms. of this bisulphide, combined with 52·1 grms. of amylene, giving 103·1 of product. If now one molecule of the bisulphide combined with one molecule of amylene, 52 grms. of the former would require 53·9 grms. of the latter, giving 105·9 grms. of product; and 51 grms. of the former would require 52·8 grms. of the latter, giving 103·8 grms. of product. The quantities actually found show that this had been in fact the proportion of combination, the numbers being as nearly in accordance as synthetical experiments of this kind allow. The substance so formed was not rendered in the least turbid on digestion with water, showing that the whole of the bisulphide was in combination. Before subjecting the compound to analysis, it was decolorized as far as possible, by being dissolved in about four times its own weight of ether, and digested with animal charcoal. After filtering, expelling the ether in a water-bath, and drying in vacuo over sulphuric acid, a product was obtained, the

analysis* of which confirmed the above synthetically derived composition.

I. 0·4721 grm. gave 0·4741 grm. of chloride of silver.

II. 0·4734 grm. gave 0·7530 grm. of sulphate of baryta.

III. 0·4239 grm. gave 0·6808 grm. of carbonic acid, and 0·2849 grm. of water.

	Calculated.	Found.		
		I.	II.	III.
C_{10}	43·64	,,	,,	43·80
H_{10}	7·27	,,	,,	7·47
S_2	23·27	,,	23·93	,,
Cl	25·82	24·73	,,	,,
	100·00			

This body may therefore be called the *Bisulphochloride of amylene*. Its formula is $C_{10}H_{10}S_2Cl$. Bisulphochloride of amylene is a transparent liquid of light yellow colour, and syrupy consistence; it is miscible in all proportions with ether, soluble in strong alcohol, especially on warming, but quite insoluble in water. Its taste, which is at first insipid, becomes very pungent and bitter; its smell is faint, and at first not unpleasant; it becomes, however, very fœtid when exposed to the air. Heated by itself, it blackens, leaving a carbonaceous residue, and giving off compounds containing sulphur as well as hydrosulphuric and hydrochloric acids. Hence neither its boiling point nor vapour-density could be determined. Its specific gravity is 1·149 at 12°C.

Action of Bisulphide of Chlorine on Ethylene.

Dry ethylene may be passed for hours through bisulphide of chlorine at temperatures varying from 0° to 100°C. without the occurrence of any appreciable chemical change, the resulting liquid being completely decomposed by water, and the products being identical with those due to the decomposition of pure bisulphide of chlorine by the same liquid.

Remembering however the readiness with which amylene combines with the same body, there can be little doubt but that on employing an arrangement by which the ethylene and bisulphide are brought together under increased pressure, the two would

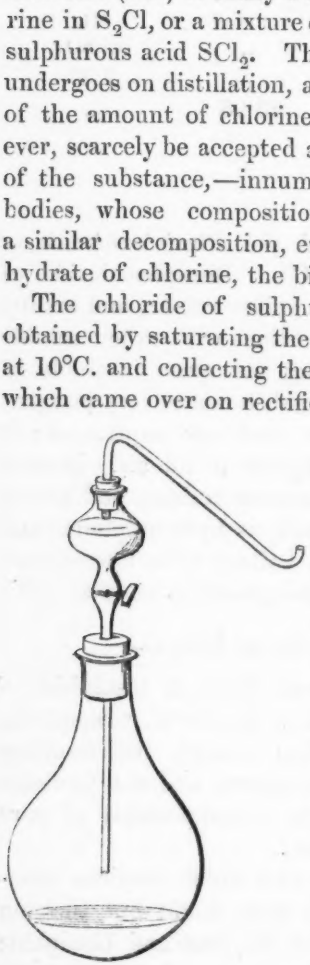
* In this and subsequent analyses, the chlorine was determined by heating with quick lime, the sulphur with carbonate of soda and chlorate of potash, the carbon and hydrogen with oxide of copper, using the ordinary precautions.

unite directly and give a product similar to the above described amylene compound.

Action of Chloride of Sulphur upon Amylene.

It has been called in question whether the instable body, chloride of sulphur, which contains chlorine and sulphur in equal numbers of atoms (SCl) is really a definite compound, or a solution of chlorine in S_2Cl, or a mixture of S_2Cl with the hypothetical analogue of sulphurous acid SCl_2. The ready elimination of chlorine which it undergoes on distillation, and the consequent continual diminution of the amount of chlorine in the successive distillates, can, however, scarcely be accepted as evidence of the heterogeneous nature of the substance,—innumerable instances occurring in which bodies, whose composition is unquestionably definite, undergo a similar decomposition, even at low temperatures (such are the hydrate of chlorine, the bisulphide of hydrogen, etc.).*

The chloride of sulphur employed in my experiments, was obtained by saturating the bisulphide of chlorine with dry chlorine at 10°C. and collecting the distillate obtained from this product, which came over on rectification between 70° and 90°C.



The action of this body upon amylene is one of very great energy; the two liquids, when brought together, hissing as when anhydrous phosphoric acid is thrown upon water. Even when the liquids are kept quite cold, a slight evolution of permanent gas attends their combination. The following arrangement was found convenient in following this reaction and examining the gas evolved.

Into a flask immersed in ice-water, 19·6 grms. of chloride of sulphur were brought. The flask was provided with a funnel-tube bearing a stop-cock, bulb, and gas-delivery tube. The bulb of the funnel-tube was filled with dry amylene. On turning the stop-cock a very little way, a portion of the amylene entered the flask;

* Carius (Ann. Ch. Pharm. cvi. 294,) has satisfactorily shewn that the solid body said to be produced by the action of chlorine upon S_2Cl contains oxygen, introduced by moisture in the chlorine.

the heat thereupon evolved, and the consequent expansion of the vapour in the flask, checked the ingress of the amylene; and the excess of permanent gas being forced to bubble through the latter, was thereby deprived of all traces of mechanically diffused vapour of chloride of sulphur. In this manner, the action was made intermittent and self-regulating. The permanent gas evolved was, however, small in quantity, and resulted from the action of the excess of chlorine upon the amylene. We shall, in fact, subsequently see that, unless very great precautions are employed, chlorine does eliminate hydrogen from amylene.

As soon as an excess of amylene had been added, the funnel-tube was removed, and the flask heated for some hours in a water-bath. The product so obtained was digested in a water-bath with dilute caustic soda, then washed with water, dissolved in ether, shaken with animal charcoal, filtered, warmed in a water-bath to expel the ether, and dried in vacuo over sulphuric acid. The product weighed 31 grms. The weight of combined amylene was therefore 11·4 grms. (neglecting the small quantity of hydrochloric acid evolved). If two molecules of the chloride of sulphur unite with one of amylene, 19·6 grms. of chloride of sulphur would combine with 13·3 grms. of amylene, giving 32·9 grms. of product.

The analysis of the body, prepared as above described, showed that such direct combination had in fact been effected.

I. 0·3723 grm. gave 0·4831 grm. carbonic acid, and 0·1786 grm. water.

II. 0·4280 grm. gave 0·5260 grm. sulphate of baryta.

III. 0·4437 grm. gave 0·7113 grm. chloride of silver.

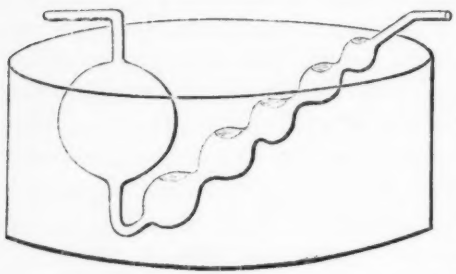
	Calculated.	Found.		
		I.	II.	III.
C_{10}	34·88	35·39	,,	,,
H_{10}	5·81	5·33	,,	,,
S_2	18·61	,,	16·86	,,
Cl_2	40·70	,,	,,	39·64
	100·00			

This body may be called the *Bichlorosulphide of amylene*. Its specific gravity is 1·138 at 14°C. Its colour is similar to that of the bisulphochloride, but deeper; its odour is more penetrating. It is miscible with ether, soluble in hot alcohol. Like the bisulphochloride, it is not volatile by itself without decomposition. Heated with alcoholic solution of caustic potash, it gives rise to

volatile products having the same physical properties, and being in all probability identical with those produced by the same reagent upon the bisulphochloride of amylene. We shall subsequently discuss the products produced in both cases; the fact, however, that the potash removes the whole of the chlorine from the bichlorosulphide, may be here noticed, because it proves that this body does not contain bichloride of amylene; for the latter body, when treated with the same reagent, gives up half its chlorine in combination with hydrogen, being converted into chloride of fusyl* ($C_{10}H_9Cl$.)

Action of Chloride of Sulphur upon Ethylene.

Ethylene acts with so much less energy than amylene upon chloride of sulphur, that it is necessary for the chloride to present as large a surface as possible to the ethylene, in order that combination may be effected. An ordinary bulb wash-tube (fig. 2) answers for this purpose. Into such a tube, chloride of sulphur was brought, and dry ethylene allowed to bubble slowly through. The bulb-tube was at first immersed in cold water. However dry the ethylene may be, and however slowly it is delivered, complete absorption never occurs, a certain quantity of the excess of chlorine in the chloride decomposing a portion of the ethylene (as in the ordinary process of forming bichloride of ethylene when the combination balloon becomes too hot or too strongly illuminated) and giving rise to hydrochloric acid. The ethylene should be allowed to pass through at the rate of about a bubble in a second. As the saturation approaches completion (a process which, with two or three ounces of the chloride, occupies about twelve hours) the liquid in the bulb-tube loses colour, changing from the garnet-red of the chloride of sulphur to the straw-yellow of the bisulphide of chlorine; at the same time heat ceases to be evolved. In order to complete the



* Here, and subsequently, I call the bodies C_4H_3 and $C_{10}H_{91}$ *vinyl* and *fusyl* respectively, reserving the names acetyl and valeryl for the oxygenated radicals $C_4H_3O_2$ and $C_{10}H_9O_2$.

re-action as far as possible, and to remove any bichloride of ethylene formed, the bulb-tube must be heated in a water-bath to 100°C. and a more rapid current of ethylene passed through for an hour or two. It seems, however, impossible, without expending an unreasonable time, to combine all the chloride with ethylene, the gradually increasing dilution of the uncombined chloride of sulphur in the liquid product of the combination being unfavourable to the exercise of its affinity. To remove the uncombined chloride of sulphur, the liquid contents of the bulb-tube were dropped into water at 80°C, repeatedly and vigorously shaken with fresh quantities of water at the same temperature, and allowed to stand for some days in contact with dilute caustic soda. The resulting product is a heavy liquid, sluggish and opaque from suspended sulphur. The latter is removed by shaking the liquid with about 100 times its volume of dry ether, filtering, driving off the ether by the heat of a water bath, redissolving in a minimum of ether, filtering, evaporating, and finally drying in *vacuo* over sulphuric acid.

I. 0·2705 grm. gave 0·2000 grm. carbonic acid, and 0·0671 grm. water.

II. 0·1844 grm. gave 0·3540 grm. sulphate of baryta.

III. 0·2957 grm. gave 0·6110 grm. chloride of silver.

	Calculated.	Found.		
		I.	II.	III.
C_4 .	18·32	20·17	,,	,,
H_4 .	3·05	2·76	,,	,,
S_2 .	24·43	,,	25·74	,,
Cl_2 .	54·20	,,	,,	51·12
	100·00			

These results agree sufficiently with the formula $C_4H_4S_2Cl_2$. The body so found is therefore a result of the direct combination of chloride of sulphur with ethylene, being the *bichlorosulphide of ethylene*. In colour, bichlorosulphide of ethylene is almost identical with the bisulphide of chlorine. Its smell is pungent and not unpleasant, resembling that of oil of mustard; its taste is astringent and similar to that of horse-radish. The small quantities of vapour which it diffuses attack the thin parts of the skin, as between the fingers and around the eyes, destroying the epidermis. If allowed to remain in the liquid form on the skin, it raises a blister. It is soluble in about fifty times its own volume of boiling ether, slightly soluble in hot, almost insoluble in cold alcohol, and

quite insoluble in water. Heated by itself, bichlorosulphide of ethylene is decomposed, giving off hydrochloric and hydrosulphuric acids, besides bodies containing carbon and sulphur, and leaving a carbonaceous residue. Its specific gravity at 13°C is 1·408.

In looking back upon these bodies $C_{10}H_{10}S_2Cl$, $C_{10}H_{10}S_2Cl_2$ and $C_4H_4S_2Cl_2$, and admitting them to be analogues of bichloride of ethylene, we seem at first at liberty to choose between two views as to their rational composition. The inorganic molecule, for instance, of the body $C_{10}H_{10}S_2Cl$ may be regarded as consisting of chloride of sulphur and sulphur. So that, preserving the above indicated analogy, its formula would be written $C_{10}H_{10}\left\{\begin{matrix}SCl\\S;\end{matrix}\right.$ or secondly, as chlorine and sulphur $C_{10}H_{10}\left\{\begin{matrix}S_2\\Cl\end{matrix}\right.$ where the two atoms of sulphur are monomolecular. Nor can the existence of such bodies as $C_4H_4S_2$ be considered hostile to the latter view, for sulphur is pre-eminently polybasic. But we are not in the same manner at liberty to choose between the formulæ $C_{10}H_{10}\left\{\begin{matrix}S_2Cl\\Cl\end{matrix}\right.$ and $C_{10}H_{10}\left\{\begin{matrix}SCl\\SCl\end{matrix}\right.$ to represent the bichlorosulphide of amylene, because the existence of $C_{10}H_{10}S_2Cl$ proves that S_2Cl is bimolecular, and hence that the second of the above formulæ, namely, $C_{10}H_{10}\left\{\begin{matrix}SCl\\SCl\end{matrix}\right.$ is alone admissible. Admitting, then, the formula $C_{10}H_{10}\left\{\begin{matrix}SCl\\SCl\end{matrix}\right.$ we must allow SCl to be monomolecular: and hence returning to the bisulphochloride of amylene, its formula must be $C_{10}H_{10}\left\{\begin{matrix}SCl\\S\end{matrix}\right.$ and not $C_{10}H_{10}\left\{\begin{matrix}S_2\\Cl\end{matrix}\right.$. The rational formula of the three bodies are hence, probably—

$C_{10}H_{10}\left\{\begin{matrix}SCl\\S\end{matrix}\right.$ Bisulphochloride of Amylene.

$C_{10}H_{10}\left\{\begin{matrix}SCl\\SCl\end{matrix}\right.$ Bichlorosulphide of Amylene.

$C_4H_4\left\{\begin{matrix}SCl\\SCl\end{matrix}\right.$ Bichlorosulphide of Ethylene.

But although the formulæ $C_{10}H_{10}\left\{\begin{matrix}SCl\\S\end{matrix}\right.$ is the most rational *statical* formula for the bisulphochloride of amylene, we shall see

that towards certain substances, it behaves like the chloride of a sulphur-containing radical $C_{10}H_{10}S_2$.

The behaviour of ethylene towards chloride of sulphur is further of interest, as affording, I believe, proof that the latter body is a definite compound, or at all events that it does not consist of bisulphide of chlorine and dissolved chlorine. For were this its composition, the free chlorine would unquestionably combine with the ethylene; but as direct experiment described before has convinced me that ethylene is almost entirely without action on bisulphide of chlorine, under the circumstances by which bichlorosulphide of ethylene is actually produced, the latter body (bisulphide of chlorine) being deprived of the excess of chlorine would remain unchanged: whereas, in fact, it is almost completely combined with the ethylene.

Moreover, in the synthesis of the bichlorosulphide of amylene, if half the chlorine in the chloride of sulphur had acted independently of the other half, the reaction would have been as follows:—

$$2\,(S_2Cl + Cl) + 3\,(C_{10}H_{10}) = 2\,(C_{10}H_{10}S_2Cl) + C_{10}H_{10}Cl_2;$$

according to which, 19·6 grms. of the chloride would have required 19·5 grms. of amylene instead of 11·4 as observed: a difference beyond the limits of observational error.

Action of ammonia upon bisulphochloride of amylene.—Aqueous ammonia may be digested with bisulphochloride of amylene for hours without any sensible change taking place.

On warming an alcoholic solution of the bisulphochloride of amylene with an alcoholic solution of ammonia, an immediate and abundant precipitation occurs. The following process was followed in tracing this reaction:—

About 50 grms. of the bisulphochloride in alcoholic solution were heated in a water-bath, in a retort connected with an inverted condenser. Ammonia evolved from an aqueous solution, and not dried, was passed through the tubulus and made to bubble through the alcoholic liquid. The gas having been passed through for several hours, the contents of the retort were allowed to stand for 24 hours. At the end of that time, they smelt strongly of ammonia. The liquid was then filtered, the insoluble portion being washed with ether. This insoluble residue was a white crystalline powder, which, after drying in *vacuo* over sulphuric acid, was not attacked by hydrochloric acid; it gave off hydro-

chloric acid without blackening, on treatment with sulphuric acid.

0·1396 grm. gave 0·3706 grm. of chloride of silver.

0·1623 grm. gave a platinum-salt containing 0·2098 grm. of platinum.

	Calculated.	Found.
NH_4 . .	33·65	34·84
Cl . .	66·35	65·67

It was therefore pure chloride of ammonium.

The filtrate from the chloride of ammonium did not contain any sulphide of ammonium. On evaporating off the alcohol from a water-bath, and adding water, a heavy liquid was separated, which, after washing with water, still contained a small quantity of chlorine. To remove this, it was heated for fie hours in a sealed tube in a water-bath at 100°C. with a fresh quantity of alcoholic ammonia. Thereupon a fresh crop of chloride of ammonia was produced. The mother-liquid was drained off, heated for some hours in a basin, in a water-bath, and precipitated with water (as long as alcohol is present, large quantities of the product are retained in solution: these may be completely precipitated by adding aqueous ammonia). The heavy liquid which separated out, after washing and mechanical drying, was dissolved in ether, digested with animal charcoal, filtered, the ether expelled by the heat of the water-bath, and the product finally dried in *vacuo* over sulphuric acid.

This substance showed on analysis the following percentage composition:—

I. 0·2134 grm. gave a platinum-salt containing 0·0123 grm. platinum.

II. 0·2129 grm. gave 0·1752 grm. water, and 0·4011 grm. carbonic acid.

III. 0·2763 grm. gave 0·2271 grm. water, and 0·5224 grm. carbonic acid.

IV. 0·2405 grm. gave 0·4790 grm. sulphate of baryta.

	Calculated.	Found.				
		I.	II.	III.	IV.	
(N) . .	0·00	0·82	,,	,,	,,	,,
C_{10} . .	50·42	,,	51·38	51·19	,,	,,
H_{11} . .	9·25	,,	9·14	9·13	,,	,,
S_2 . .	26·89	,,	,,	,,	27·15	,,
O_2 . .	13·44	,,	,,	,,	,,	11·72

The ammonia is evidently present as an impurity only, probably either as chloride of ammonium, or as bisulphide of fusylamine, the latter supposition being the more probable, owing to the excess of carbon found; in either case, the amount of oxygen would be increased by its removal. The body formed is the *hydrated oxide of bisulphamylene* $C_{10}H_{10}S_2O.HO$, its formation taking place according to the equation—

$$C_{10}H_{10}S_2Cl + NH_4O.HO = NH_4Cl + C_{10}H_{10}S_2O.HO$$

The alcohol employed serves only as a solvent medium, and remains chemically passive.

The formation of this body under the circumstances above-mentioned, namely, the assumption of water in its generation, is another and instructive example of hydration by means of ammonia, a phenomenon which is generally significant of the formation of an alcohol.

The hydrated oxide of bisulphamylene is not volatile without decomposition; when heated, it emits a most fœtid odour, blackens, and leaves a carbonaceous residue. Its specific gravity at 8°C. is 1·049. It is quite transparent, viscid and of an orange-yellow colour: its smell is faint and meaty. It is insoluble in water, but miscible with bisulphide of carbon, ether and absolute alcohol.

The action of alcoholic caustic potash upon bisulphochloride of amylene is similar to that of ammonia.

On heating the bisulphochloride for a few minutes in a water-bath with an excess of alcoholic caustic potash, the whole of the chlorine separates out as chloride of potassium, the hydrated potash giving up both oxygen and water, and converting the bisulphochloride into the hydrate of the oxide of bisulphamylene.

$$C_{10}H_{10}S_2Cl + KO,HO = C_{10}H_{10}S_2O.HO + KCl$$

Five grammes were treated in this way with alcoholic potash. The excess of alcohol being expelled on a water-bath, the residue was washed with water and dried in *vacuo* over sulphuric acid.

0·3225 grm. gave 0·2759 grm. water and 0·6050 grm. carbonic acid.

	Calculated.	Found.
C_{10} . .	50·42	51·16
H_{11} . .	9·25	9·50
S_2		
O_2		

The water with which the liquid had been washed did not contain any sulphide of potassium.

The liquid obtained by caustic potash is, therefore, identical with that formed by ammonia. Aqueous caustic potash, like aqueous ammonia, does not exert any action upon bisulphochloride of amylene.

As bisulphochloride of amylene is converted into a hydrated oxide by the hydrated oxide of an alkaline metal, so is it converted into an anhydrous oxide by an anhydrous metallic oxide. This is the case, even when water is present, so long as the latter is not in chemical combination with the oxide employed; for example:—

A large excess of oxide of lead (PbO) was digested over a water-bath for several hours with an alcoholic solution of bisulphochloride of amylene, the alcohol being continually renewed as it evaporated. As soon as a drop of the solution showed, on testing, that the whole of the chlorine had been removed, fresh alcohol was added, the product filtered, the filter washed with alcohol, and the filtrate evaporated and dried in *vacuo* over sulphuric acid. An almost colourless heavy liquid was obtained, which, after drying, gave the following percentage composition:

I. 0·2576 grm. gave 0·2094 grm. water and 0·5187 grm. carbonic acid.

II. 0·3222 grm. gave 0·6866 grm. sulphate of baryta.

	Calculated.	Found.	
		I.	II.
C_{10} .	54·54	54·92	,,
H_{10} .	9·09	9·03	,,
S_2 .	29·09	,,	29·24
O .	7·28	,,	,,
	100·00		

This agrees with the composition of *oxide of bisulphamylene*. $C_{10}H_{10}S_2O$:—the oxide of lead having simply substituted oxygen for chlorine.

$$C_{10}H_{10}S_2Cl + PbO = C_{10}H_{10}S_2O + PbCl$$

The oxide of bisulphamylene is an almost colourless, yellowish, sluggish, transparent liquid of nauseous taste and smell: it is not volatile without decomposition. It is miscible with alcohol, ether

and bisulphide of carbon, immiscible with water; its specific gravity is 1·054 at 13°C.

It is noteworthy that in the preparation of the hydrated oxide of bisulphamylene described before, if the solution of potash in alcohol contained a very large quantity of potash, a product was obtained containing an amount of carbon intermediate between that of the simple oxide and the hydrated oxide. This is undoubtedly due to the actual formation of some oxide by the hydrated potash.*

The difference in chemico-negativism of the chlorine and sulphur in the bisulphochloride of amylene and the consequent introduction of oxygen in place of the former element, evinced in the above reactions, suggests at once the possibility of introducing an organic group in place of the chlorine from some compound in which such group is itself chemico-negative. The ethylates of the alkalis offer us examples of such bodies, and the discoverer of zinc-ethyl has placed a further instance of the same class in the hands of chemists.

Nevertheless, the first of the reactions indicated does not appear to take place under ordinary circumstances. If ethylate of soda and bisulphochloride of amylene be warmed together, the two react with considerable energy. In an experiment of this kind, an excess of ethylate of soda was warmed in a flask with bisulphochloride of amylene: chloride of sodium was formed. The resulting liquid was shaken with water, and the product formed was extracted by ether. After filtering, evaporating, washing and drying the ethereal solution, it was analysed. (It did not contain chlorine, and the wash-water was free from sulphur.)

I. 0·3424 grm. gave 0·6878 grm. carbonic acid and 0·2787 grm. water.

In a second portion from another quantity, in the preparation of which the utmost pains were taken to leave the ethylate of potash free from hydrate of potash:

II. 0·3759 grm. gave 0·7559 grm. carbonic acid and 0·2974 grm. water.

These results agree far better with the simple oxide of bisulphamylene than with the ethylate of oxide of bisulphamylene sought.

* This anhydrous oxydation harmonizes with the fact that hydrated potash dissolved in amylic alcohol, reacts upon iodide of ethyl, forming ethylate of amyl. (See *Phil. Mag.*, September, 1857.)

	$C_{10}H_{10}S_2O$	Found. I.	II.	$C_{10}H_{10}S_2O.C_4H_5O$
C .	54·54	54·78	54·85	57·15
H .	9·09	9·05	8·70	10·20

Hence the ethylate of potash does not act as the hydrate of potash, that is the oxide of ethyl does not combine with the oxide of bisulphamylene on the formation of the latter. In other words, there is no *double ether* formed. The ethylate of potash, in short, has the same action as oxide of potassium would undoubtedly have and as we have already seen the oxide of lead to possess.

In consequence of this negative result, I have not submitted the bisulphochloride to the action of other alkaline ethylates.

We have already discussed the action of hydrated potash upon bisulphochloride of amylene at temperatures below 100°C. If, however, after the two have reacted at this temperature, the product be submitted to distillation in presence of an excess of potash, further decompositions are effected. In tracing these, the following method was pursued. Caustic potash was dissolved in alcohol and evaporated so far that it solidified on cooling; it was then brought into a tubulated retort connected with a very well cooled condenser, and heated till it became quite fluid. Bisulphochloride of amylene was allowed to drop upon it through a funnel-tube passing through the tubulus and provided with a stop-cock. The temperature was at first moderated, the first action (the formation of the hydrated oxide of bisulphamylene) being determined at low temperatures. Increased heat was gradually applied until the lower part of the retort became red-hot, oily drops still continuing to pass over. When the distillation was complete, water was added, and the light liquid which thereupon separated out was washed with water and dried over chloride of calcium. The volume of product so obtained was about two-thirds that of the amylene compound employed. On rectification, it began to boil between 50° and 60°C. The boiling point remained for some time stationary between 110° and 115°C, after which it rose rapidly. There were consequently, at least, three liquids present; fortunately, however, their respective boiling-points were so far apart as to allow of their separation by rectification.

The more volatile portion was submitted to rectification by itself, the distillate being collected in an artificially cooled condenser. A considerable product was obtained, having the fixed boiling-point 39°C.

I. 0·1635 grm. gave 0·5093 grm. carbonic acid and 0·2132 grm. water.

II. 0·1751 grm. gave 0·0362 grm. sulphate of baryta.

III. 0·1743 grm. gave only a trace of chloride of silver.

Calculated.		Found.	
	I.	II.	III.
C_{10} . .	84·95	,,	,,
H_{10} . .	14·48	,,	,,
(S) . .	,,	2·83	,,
(Cl) . .	,,	,,	Trace

This body was therefore amylene; the presence of sulphur is due to the body next to be described, with which the amylene was contaminated, and which could not be completely separated by rectification.

The portion of the original distillate which came over between 110° and 115°C. was next submitted to rectification.

Its boiling-point, after four rectifications, became constant at 112°C.

0·2687 grm. gave 0·5746 grm. of sulphate of baryta.

0·2581 grm. gave 0·5615 grm. of carbonic acid and 0·2276 grm. of water.

	Calculated.	Found.	
		I.	II.
S_2 . .	31·68	29·29	,,
C_{10} . .	59·40	,,	59·33
H_9 . .	8·91	,,	9·84
	99·99		

This substance, the bisulphide of fusyl $C_{10}H_9S_2$ is perfectly colourless and transparent, miscible in all proportions with ether, soluble in alcohol, insoluble in water. Its smell is not disagreeable. Its specific gravity is 0·880 at 13°C.

The analysis given would not by itself be conclusive as to the composition of the above-described body. Both bisulphide of amyl and amyl-mercaptan as well as bisulphide of amylene would give analytical results according with the above within the limits of analytical error. My reasons for assigning to it the above compositions are: (1) its boiling-point, bisulphide of amyl boiling at 250°C.; (2) its indifference both alone and in alcoholic solution

towards both protoxide of mercury and acetate of lead, with which amyl-mercaptan combines with great energy; and (3) its being a volatile liquid soluble in ether and alcohol, bisulphide of ethylene being non-volatile and insoluble in these media.

Besides these two products, bisulphochloride of amylene gives rise in presence of caustic potash at high temperatures to other volatile products of boiling-points above 112°C. which I have not examined.

None of the bodies described above became solid at −18°C.

A description of some derivatives from the other two sulphur-chlorine compounds above described, $C_{10}H_{10}S_2Cl_2$ and $C_4H_4S_2Cl$, as well as of some direct derivatives from the two olefines, I reserve for a future communication.

Since writing the above, I have succeeded in combining ethylene with bisulphide of chlorine in such a manner as leaves no doubt that the product is $C_4H_4S_2Cl$. If this be the case, there can be little doubt but that such a body will give rise to a series of compounds similar to those considered above, belonging to the corresponding amylene-olefine.

XIV.—*Note on Paviin.*

By G. G. Stokes, Sec. R. S.,

LUCASIAN PROFESSOR OF MATHEMATICS IN THE UNIVERSITY OF CAMBRIDGE.

The crystallizable substance, the existence of which in the bark of the horse-chestnut I noticed in a former communication to this Society,* and to which I gave the name paviin, together with æsculin which it closely resembles in its properties, may be thus prepared.

A decoction of the bark having been made, and allowed to grow cold, there is added a persalt of iron, such as pernitrate, until on testing a sample by the addition of ammonia, the precipitate separates at once in distinct flocks, leaving a bright pale yellow highly fluorescent fluid, giving a mixture which filters readily. The whole is then precipitated by ammonia and

* Chem. Soc. Qu. J. vol. xi. page 17.

filtered; about one-fourth of the ammoniacal filtrate is precipitated with acetate of lead, avoiding an excess, ammonia being added if required; the mixture is restored to solution by the addition of acetic or dilute nitric acid, added to the remainder of the first filtrate previously acidulated; the whole precipitated by ammonia and filtered; and the filtrate precipitated by ammoniacal acetate of lead and filtered. The two precipitates are collected separately, and treated with acetic acid until they are dissolved, or at least wholly broken up, filtered if need be, and set aside in a cool place. The second precipitate yields æsculin, which makes its appearance as a light precipitate, appearing under the microscope to consist wholly of minute needles. The first precipitate yields paviin, which ordinarily crystallizes in tufts of very long slender silky crystals. When the solution is comparatively impure, it sometimes crystallizes very slowly in shorter and far thicker crystals. The crystallization of paviin is sometimes remarkably facilitated by dropping in a very minute portion of the substance from a previous preparation. When the crystallization, whether of æsculin or of paviin, ceases to progress, the mass of crystals is thrown on a filter, drained, and pressed out. The mother liquors being similarly treated by partial precipitation, yield additional quantities of the substances.

The æsculin thus obtained, after merely pressing out the crystals, without washing, is usually snow-white. The paviin, which appears to be naturally slightly yellow, is often mixed with a brown product of decomposition of other substances, which however, being insoluble in water, is of little consequence.

The properties, especially the optical properties, of paviin, so far as I have observed, appear to be absolutely identical with those of fraxin, a crystallizable substance discovered in the bark of the ash by the Prince of Salm-Horstmar,* who has favoured me with a specimen. The substances would seem to be identical,† but analyses are yet wanting. Accordingly, it is unnecessary to describe the properties of paviin. I will limit myself to two observations relative to horse-chestnut bark, in which optics come in aid of chemistry.

The quantity of paviin contained in horse-chestnut bark is larger than I had at first imagined. I find that in order to match

* Pogg. Ann. c. 607.

† I find fraxin, like paviin, to be slightly soluble in ether, at least washed ether.

the tint of the fluorescent light of a decoction of horse-chestnut bark by a mixed solution of æsculin and paviin, the substances must be present in the proportion by weight of about 3 to 2. The relative proportion of paviin as compared with æsculin actually obtained is liable to be much less than this, which arises, I believe, from the circumstance that paviin, from its somewhat stronger affinities, is less easily separated than æsculin from certain readily decomposed substances present in the decoction.

The production of æsculetin from æsculin may be elegantly followed by combining the optical and chemical properties of the substances. A solution liable to contain æsculetin is acidulated, if not already acid, and agitated with about an equal volume of ether. The ether withdraws the æsculetin, and when the whole is examined by daylight transmitted through a deep manganese purple glass (Phil. Trans. 1853, p. 385), the æsculetin shows itself by the strong fluorescence of the ethereal solution. In this way it is easy to tell what acids give rise to the formation of æsculetin by boiling a teaspoonful of water containing, say, the hundredth of a grain of æsculin with the acid to be tried. It is easy, too, to demonstrate the absence of æsculetin in the bark itself, and its presence in a decoction which has stood some time.

In describing an analysis of horse-chestnut bark not yet complete, Rochleder mentions a *nearly neutral** crystallizable substance which *accompanies æsculin in small quantity*. If this be paviin, as seems probable, the subject is at present in the hands of Rochleder, who has also undertaken the analysis of fraxin.

XV.—*On the Absorption of Hydrochloric Acid and Ammonia in Water.*

By Henry E. Roscoe and William Dittmar.

The important investigations of the relations exhibited in the absorption by water of the more commonly occurring gases, lately made by Bunsen† and his pupils, have established the truth of the law originally enunciated by Henry and Dalton, according to which the quantity of a gas dissolved in a liquid at a constant

* Gmelin's Handbuch, vol. 8 (1858), p. 25.

† See Bunsen's Gasometry. London; Walton and Maberly. Page 128.

temperature is directly proportional to the pressure, whether total or partial, under which the absorption takes place.

The theoretical explanation given by Dalton of this simple relation, according to which the law must be considered as a special case of the law of Boyle, can scarcely be adopted at the present day. It is, on the contrary, far more probable, as Bunsen believes, that the general law expressing the true relation between the amount of absorbed gas and the pressure, is an extremely complicated one, which only appears to possess the simplicity expressed by Dalton's law between certain narrow limits of pressure and temperature.

There are especially two conditions under which the deviations from this simple but less general law may become perceptible; in the first place, namely, under pressures and at temperatures at which the gas approaches the point of liquefaction; secondly, in cases in which the so-called chemical attractions begin to exert their influence.

In order to throw some little light upon the phenomena of gas-absorption occurring under one or both of these conditions, we have, in the following communication, to detail the results of experiments made upon the absorption of hydrochloric acid and ammonia by water, under varying conditions of pressure and temperature.

A. EXPERIMENTS WITH HYDROCHLORIC ACID.

I.—*Relation between the amount of Hydrochloric Acid Gas absorbed in Water at* 0° C. *and the pressure under which the absorption occurs.*

In few of the numerous experiments given by Bunsen in proof of the truth of Dalton and Henry's law, have the alterations in the amount of the absorbed gas been effected by the variations of the total pressures, almost all the examples showing the applicability of the law being proved for partial pressures with mixtures of different gases. Experiments made by one of us,* showed on the other hand, that chlorine gas in its behaviour to water forms an exception to the general rule, inasmuch as it was found that the amount of dissolved chlorine is not only dependent upon the partial pressure, but is also influenced by the chemical nature of the diluting gas. As a similar disturbing presence-action of the diluting substances might possibly occur in the two gases under

* Roscoe, Chem. Soc. Qu. J., vol. iii, p .14.

investigation, it was advisable to determine the quantity of gas absorbed under different amounts of direct pressure. For this purpose, we have made use of a method by means of which we are enabled to determine the solubility of hydrochloric acid and ammonia under direct pressures varying from a few millimeters to two meters of mercury.

The essential features of this method consist in saturating a certain quantity of water contained in a bulb-apparatus, of known weight and capacity, with the pure gas at a given temperature, and under a given pressure. When the liquid was saturated, the bulb was hermetically sealed, the total weight determined, and the amount of contained gas ascertained by analysis. In this way all the data necessary for the calculation are obtained.

According as the determination was required under pressures equal to, less than, or greater than the atmospheric pressure, certain special arrangements were adopted.

For the purpose of determining the solubility of hydrochloric acid gas under the ordinary atmospheric pressure, a moderate current of gas evolved and purified with all due precautions, was passed into from 0·5 to 2 grammes of water contained in the glass bulb, apparatus, fig. 1, of known weight and capacity (from 10 to 15 cbc.), joined to the washing bulbs of the evolution flask by sheet caoutchouc tubes. For obvious reasons, 0°C was the temperature chosen as that at which all the pressure determinations should be made, and the bulb-vessel was therefore plunged into a bath of finely pounded and melting ice. In a series of preliminary experiments, we had determined the time which elapsed from the commencement of the evolution until the water in the bulb was saturated, and had attained the constant temperature of the bath. To ensure the establishment of the required absorptiometric equilibrium, we allowed, in the actual determinations, the passage of the gas to continue for half an hour after this point of saturation had been attained. The bulb was then completely closed by first pressing the sheet caoutchouc joining nearest the evolution-vessel, and then that on the limb from which the gas escaped into the atmosphere, with suitable screw-clamps. After having separated the bulb-vessel from the other parts of the apparatus, it was cooled down in a freezing mixture to a temperature considerably below 0°C, and hermetically sealed at *bb*, before the blow-pipe.

FIG. 1.

The barometric pressure was then observed, the bulb and its contents accurately weighed, and the total hydrochloric acid determined by volumetric analysis with silver, the bulb being broken under water, and an aliquot portion of the resulting acid liquid employed for analysis. From these data the weight of hydrochloric acid absorbed by one gramme of water is easily obtained. The capacity of the bulb and the volume of liquid being known, the weight of gaseous hydrochloric acid contained above the liquid can be found, and then the weight of dissolved hydrochloric acid and the weight of the water can be calculated from the direct observations.

In order more clearly to illustrate the details of the method, we give all the data obtained in one experiment for the determination of the solubility of hydrochloric acid at 0° C. and under a barometric pressure of 0·7398 meters of mercury.

Weight of apparatus empty = 9·5532 grms.

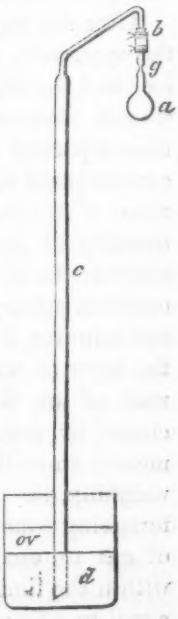
Capacity of apparatus to *bb*, fig. 1, = 6·5 cbc.

Weight of apparatus + contents at 0·76^{m} and 15 °C = 10·9768 grms.

Ditto + contents + displaced air = 10·9848 grms.

The total content of the apparatus was diluted with water to 183·1 cbc., and of this acid liquid 50 cbc. were taken for analysis. This quantity required 4·875 × 108 milligrammes of silver for complete precipitation; hence the total amount of hydrochloric acid is 0·6515 grm. In order to obtain the amount of dissolved hydrochloric acid, we must subtract from this total quantity the weight of 5·4 cbc. (the capacity of apparatus—volume of liquid) of gaseous acid = 0·0085 grm. We then have 0·6430 grm. of hydrochloric acid absorbed in 1·4316 − 0·6515 = 0·7801 grms. of water; or 1 gramme of water absorbs, under the circumstances of the experiment, 0·8241 grm. of hydrochloric acid, which, measured at 0° C., and under a pressure of 0·76^{m}; occupies a volume of 405·3 cbc.

FIG. 2.



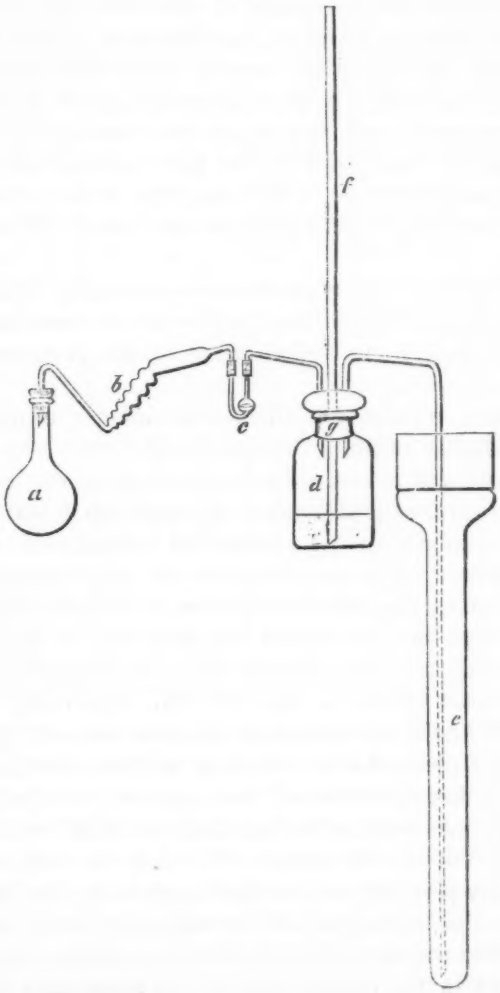
When the solubility of the gas under pressures less than one atmosphere was required, the following modification of the method was employed. In place of the apparatus, fig 1, a simple bulb, *a*, fig. 2,

of about 10 cbc. capacity, blown on to the end of a glass tube, was used as the saturating vessel. Into this weighed bulb, containing about 2 grms. of water, pure hydrochloric acid gas was passed at a temperature of — 15° C. until the liquid was completely saturated. The delivery tube through which the gas entered was then removed, and, whilst the bulb still remained in the freezing mixture, a carefully prepared tube of sheet-caoutchouc, *b* fig 2, containing a spiral of platinum wire, was made fast to the end of the bulb-tube. This caoutchouc connected the bulb by a moveable, but perfectly air-tight joint with a vertical barometer-tube, *c*, divided into millimeters and previously filled with the gas, the lower end dipping under mercury. The freezing mixture was now removed from the bulb, and the temperature of the liquid gradually rose, whilst the dissolved gas was rapidly disengaged, making its escape from the lower end of the barometer-tube, *b*, through the mercury into a layer of water, *w*, placed to receive it. As soon as the escaping gas was seen to be completely absorbed by the layer of water, so that absence of any trace of air was ensured, the liquid in the bulb was carefully warmed by means of a water-bath to some temperature above 0° C. which was more nearly regulated by the amount of pressure under which the solubility had to be determined.

After the requisite quantity of gas had thus been expelled from the apparatus, the bulb was again plunged into a bath of melting ice, and the liquid allowed to attain the temperature of zero. No sooner, however, does the temperature of the liquid diminish, than a portion of the gas above the water is again absorbed, and a consequent rise of the column of mercury in the barometric-tube *c* occurs, the amount of this rise depending upon the quantity of gas previously expelled. By continually shaking the bulb the level of the mercury in the tube was soon brought to a constant point; and after the meniscus had remained stationary for ten minutes, during which time the liquid was constantly agitated, the layer of water was removed; and the height of the column read off on the divided scale. The bulb was then completely closed by pressing the caoutchouc tube with a screw-clamp, removed from the apparatus and hermetically sealed at *g*. After weighing, the analysis and calculations were made exactly as in the foregoing example. In this way, by allowing different quantities of gas to escape, the saturation may be effected under pressures within the limits of the barometric variation, or under pressures equal to a few millimeters of mercury.

The determinations of the solubility of hydrochloric acid under pressures greater than that of the atmosphere, were made by simply leading the gas through water contained in the bulb apparatus, fig. 1, under the required pressure. This pressure was obtained by means of the arrangement represented in fig. 3. The gas issuing

Fig. 3.



from the bulb-apparatus *c* enters the vessel *d*, and thence has to pass through a column of mercury *e* of the requisite depth. The

exact pressure was measured by the rise of mercury in the divided tube *f*, fixed tightly by means of a massive caoutchouc stopper into the vessel *d*, which also serves as an air-chamber to equalise the variations of pressure. The difficulty of obtaining joints which will stand a pressure of several atmospheres, and yet can be perfectly closed by screw-clamps, was overcome by the following simple arrangement. The saturation bulb was joined to the other parts of the apparatus by means of well-made sheet-caoutchouc tubes, which were so attached that the ends of the glass tubes were left about 10 mm. apart; outside this middle portion of the caoutchouc, a piece of copper or brass foil, about 20 mm. broad, was tightly wrapped, and this copper was overlapped at each end of the caoutchouc with strips of lead foil also about 20 mm. broad, the whole arrangement, with the exception of the central part of the copper foil, being then tightly bound round with soft copper wire.

Thus connected, the apparatus was moveable within certain limits, could be perfectly closed by the screw-clamps at pleasure, and was absolutely air-tight under pressures up to three atmospheres.

In the actual experiments, the gas was allowed to pass through the bulb apparatus, escaping from below the column of mercury *e*, until the liquid had attained the temperature of the ice-bath, and was perfectly saturated with gas. The variation of the level of the column of mercury in the manometer tube *f* was continually observed during the whole course of the experiment, the mean height being taken as giving the pressure of the gas; the apparatus was then closed on the side of the evolution vessel by a screw-clamp; the height of the mercury again noted; and the second limb of the bulb closed in like manner. The vessel containing the saturated liquid was now removed from the other part of the apparatus and plunged into a freezing mixture, composed of two parts of crystallized chloride of calcium, and three parts of finely powdered ice. As soon as the liquid had attained the temperature of the bath ($-30°$ C) the tension of its vapour became less than the barometric pressure, and the bulb-apparatus was hermetically closed before the blow-pipe. After regaining the ordinary atmospheric temperature, the bulb thus filled was weighed, and the contents analysed in the manner already described, care being taken again to cool the liquid in a freezing mixture before opening under water.

The results of ten experiments, conducted according to these three different methods, are thrown together in the following Table.

TABLE I.

At the temperature 0° C. one gramme of water absorbs G grammes of hydrochloric acid gas under the partial pressure of* P meters of mercury.

No.	1	2	3	4	5	6	7	8	9	10
P.	0·058	0·321	0·569	0·735	0·737	0·755	0·932	0·937	1·263	1·270
G.	0·614	0·746	0·796	0·824	0·821	0·827	0·851	0·851	0·890	0·887

By means of these direct observations, the values in Table II. were obtained by graphic interpolation. From these, as also from the curve HCl (Fig. 4), we obtain a clear idea of the relation between the amount of hydrochloric acid absorbed by water at 0° C. and the pressure under which the absorption occurs.

TABLE II.

P.	G.	P.	G.	P.	G.	P.	G.
0^{m}·06	0·613	0·14	0·681	0.35	0·751	0·75	0·824
0·07	0·628	0·15	0·686	0.40	0·763	0·80	0·831
0·08	0·640	0·175	0·697	0.45	0·772	0·90	0·844
0·09	0·649	0·20	0·707	0.50	0·782	1·00	0·856
0·10	0·657	0·225	0·716	0.55	0·791	1·10	0·869
0·11	0·664	0·25	0·724	0.60	0·800	1·20	0·882
0·12	0·670	0·275	0·732	0.65	0·808	1·30	0·895
0·13	0·676	0·30	0·738	0.70	0·817		

A glance at the numbers in Table II, or at the curve HCl (Fig. 4), renders evident the singular fact that the amount of hydrochloric acid gas absorbed by water at 0°C. alters but very slightly with the pressure, a variation of pressure from 1 meter to 0·5 meter producing a diminution in the quantity of absorbed gas of only 8·7 instead of 50 per cent. Hence it is seen that in this case the law of Henry is not even approximately applicable.

A plausible explanation of the slight influence exerted by pressure on the quantity of hydrochloric acid dissolved by water at

* By partial pressure we here signify the total pressure under which the absorption occurs, *minus* the tension of aqueous vapour at 0°C.

0°C. might be given by supposing that the absorbed gas consists of two portions, one of which is chemically combined with the water, and the other absorbed in accordance with the law. A large portion of the curve HCl (fig. 4) being identical with the straight line *cd*, would seem to bear out this supposition, but the experiments made at pressures below 0·60^{m} show that the curve deviates from the straight line, and that, therefore, this hypothesis must be abandoned.

We must, however, allow that some portion of the dissolved hydrochloric is independent of the pressure, as the gas cannot be totally expelled by boiling, or displaced, as we shall presently show, by an atmosphere of another gas.

II.—*Relation between the Amount of Hydrochloric Acid Gas absorbed in Water under the ordinary Atmospheric Pressures, and the Temperature at which the Absorption occurs.*

All these determinations were made exactly according to the ethod already described for 0° C. under the atmospheric pressure. The temperatures above 0° C. were obtained by placing the apparatus (fig. 1) in a water-bath, which we succeeded in keeping to within $\frac{1}{10}$°C. of the required temperature, by means of the usual arrangements. The indications of the thermometers we employed were corrected by a complete series of comparisons with a normal instrument from the Kew Observatory, kindly lent by Dr. Joule.

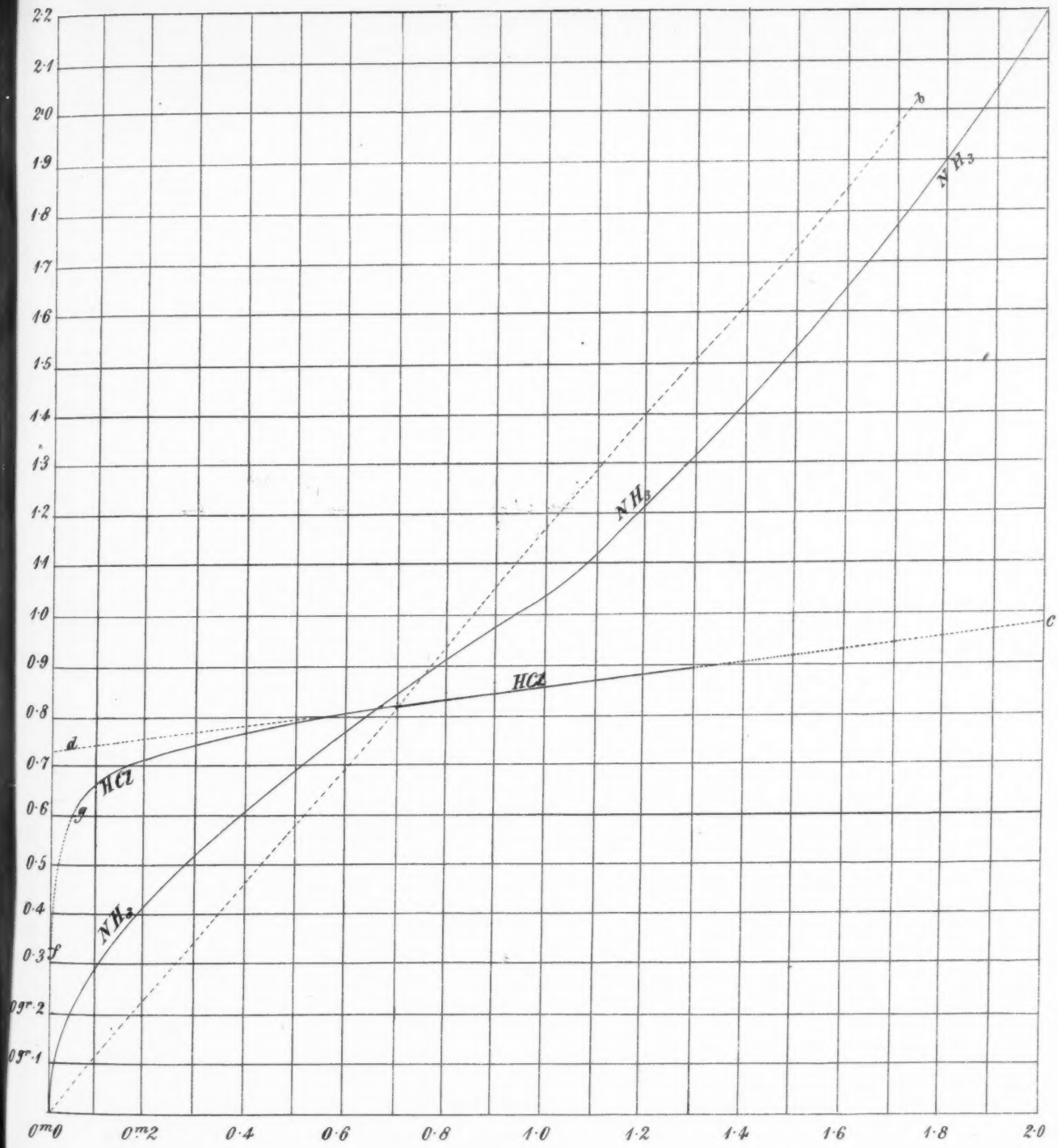
The following Table III contains the results of these experiments:—

TABLE III.

One gramme of water absorbs, under the atmospheric pressure B, and at the temperature t°C. G grammes of hydrochloric acid gas.

No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
B.	0·760	0·762	0·754	0·754	0·739	0·753	0·750	0·756	0·757	0·753	0·758	0·767	0·756	0·766	0·766
t°	4°·7	4°·8	7°·2	7°·2	16°·0	16°·0	24°·2	24°·4	24°·5	35°·3	35°·4	43°·5	43°·5	59°·2	59°·2
G.	0·799	0·801	0·790	0·792	0·738	0·741	0·697	0·696	0·697	0·653	0·657	0·619	0·627	0·562	0·566

The reduction of these numbers to 0·760^{m}., or any other constant pressure, would have entailed for each temperature a similar series of pressure experiments as that made as 0°. Con-


2·2
2·1
2·0
1·9
1·8
1·7
1·6
1·5
1·4
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0·9
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0·6
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0·4
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0gr·2
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0m0
0m2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
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2·0
a
b
c
d
e
f
g
NH3
HCl
NH3
HCl
NH3

Fig. 4.

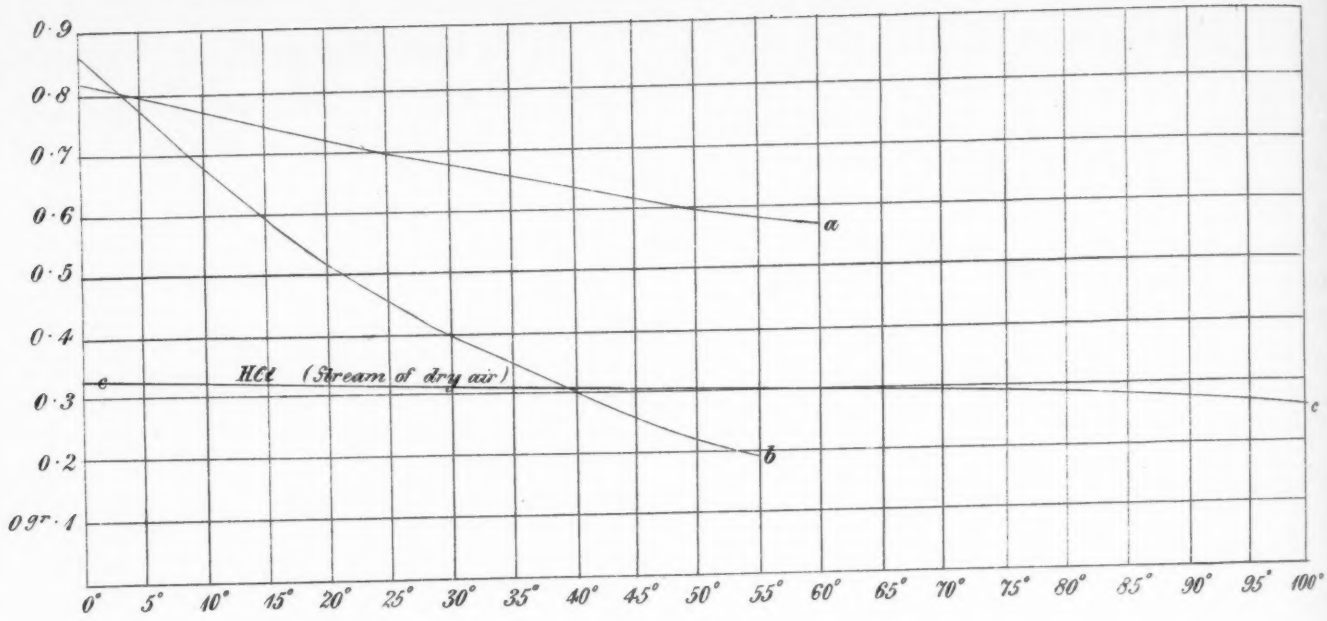
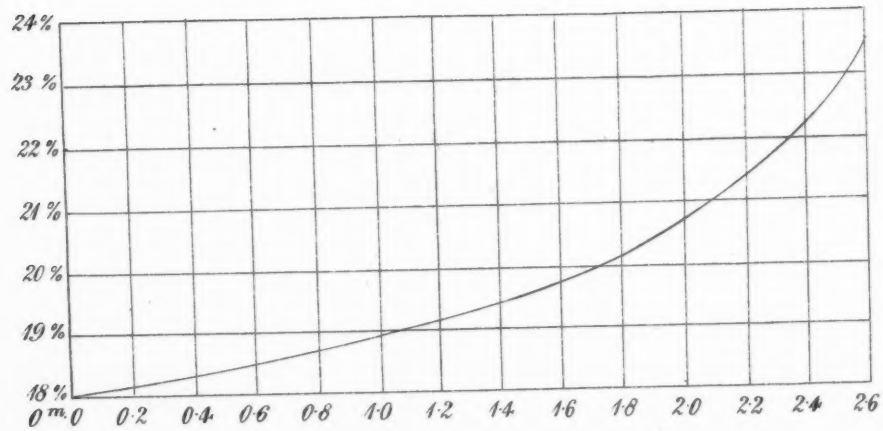

0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0gr·1
a
HCl (Stream of dry air)
c
b
c
0°
5°
10°
15°
20°
25°
30°
35°
40°
45°
50°
55°
60°
65°
70°
75°
80°
85°
90°
95°
100°

Fig. 5.


24%
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0·2
0·4
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1·6
1·8
2·0
2·2
2·4
2·6

Fig. 7.

sidering, therefore, the slight influence of pressure at this temperature, we have thought it best to leave the experimental results uncorrected, supposing that they were all made at 0·760^{m}. The numbers in the following Table IV give the weights in grammes (G.) of hydrochloric acid absorbed under the barometric pressure 0·760^{m} by 1 grm. of water at the temperatures t°, the values being obtained by graphical interpolation from the direct experimental results in Table III.

TABLE IV.

t° C.	grms.	t° C.	grms.	t° C.	grms.	t° C.	grms.
0°	0·825	16°	0·742	32°	0·665	48°	0·603
2°	0·814	18°	0·731	34°	0·657	50°	0·596
4°	0·804	20°	0·721	36°	0·649	52°	0·589
6°	0·793	22°	0·710	38°	0·641	54°	0·582
8°	0·783	24°	0·700	40°	0·633	56°	0·575
10°	0·772	26°	0·691	42°	0·626	58°	0·568
12°	0·762	28°	0·682	44°	0·618	60°	0·561
14°	0·752	30°	0·673	46°	0·611		

The curve *a* (Fig. 5) represents the relation between the temperature taken as abscissa, and the weight of gas absorbed under 0·760^{m} taken as ordinate.

The foregoing experiments, as well as many older observations, show conclusively that the laws regulating the absorption of hydrochloric acid in water are totally different from those which the other gases obey. When aqueous solutions of other gases, even the most soluble, such as ammonia, are heated, the dissolved gas is quickly displaced, until, when the water has been boiled for a short time, all the absorbed gas has disappeared from solution. In accordance with the law of Dalton and Henry, we know, too, that most gases are expelled completely from water at temperatures lower than 100° C., when a constantly renewed atmosphere of a foreign gas is brought into contact with the solution. The greater or less solubility of the gas effects in no way this expulsion, ammonia being completely driven from solution by a current of atmospheric air.

Dalton long ago showed that hydrochloric acid forms an exception to this rule, and Bineau corroborating these results, proved that aqueous hydrochloric acid, whether saturated or otherwise, if boiled under the ordinary atmospheric pressure, at last attains a

point at which anhydrous acid and water distil over in the same proportions in which they are contained in the residue. The composition of the aqueous acid thus obtained was found by Bineau to correspond closely with the formula HCl + 16HO. The same chemist further found, that this aqueous acid, when exposed at ordinary atmospheric temperatures to dry air, continues to lose water until a constant composition is again attained, which is represented by the atomic relation HCl + 12 HO. From these observations of Bineau it would appear, that hydrochloric acid forms at least two hydrates which may be regarded as chemical compounds, and that all aqueous solutions of this gas may be supposed to be mixtures of one or both of these hydrates, with excess either of acid or water. It is, however, also possible that the fact that these two acids have an atomic composition is purely accidental, and does not therefore imply the existence of any points of maximum attraction sufficient to justify the assumption of definite chemical combination. The constancy of the boiling point of the aqueous acid containing HCl + 16 HO, as observed by Bineau, in no way proves the existence of a chemical compound, as this same result might equally well ensue from simple physical causes. Thus, for instance, it is possible to conceive of a mixture of two liquids whose vapours possess at the same temperature different tensions, such that, when ebullition commences at a given temperature and under a corresponding pressure, the proportion between the weights of the two vapours distilling over is the same as that in which the liquids have been mixed; and that, therefore, the mixture boils at a constant temperature, without undergoing any change in its composition. We thus see that, under given circumstances of temperature and pressure, a mixed liquid may act, as regards boiling point, like a uniform chemical combination; the latter must, however, retain its properties within a certain range of varied physical conditions, when the mixture is unable to do so. According to received ideas, a chemical compound may be defined as a substance, whose constituents are united in atomic proportions, able as a whole to withstand a certain amount of change of physical conditions, without alteration. If, then, Bineau's acids are really definite hydrates, they must be capable of existing under pressures greater or less than that of the atmosphere, and aqueous hydrochloric acid distilled under such circumstances, ought likewise to attain a constant composition of HCl + 16HO.

In order to determine which of these two hypotheses is the correct one, we, in the first place, repeated Bineau's experiments, for the purpose of examining what were the actual deviations from the theoretical results, the supposition of atomic relations not being admissible in the case in question, owing to the accuracy of the analytical results, unless a very close approximation is obtained.

In the first series of experiments we boiled a liquid which contained 18·5 per cent. of anhydrous acid in a retort, collecting portions of the residue from time to time, and analysing them by means of silver. The boiling point of the liquid soon became constant at 110° C. and after a considerable portion of the acid had distilled over, the residue contained 20·16, and after further distillation 20·21 per cent. of hydrochloric acid. A second series of experiments with an acid containing 24·8 per cent. HCl showed that when the liquid was reduced to $\frac{6}{10}$ of its original volume, the residue had a composition of 20·39 per cent., and that when half the liquid had been distilled, the remainder contained 20·29 per cent. of anhydrous acid. In a third experiment, the composition both of the distillate and residue of an acid which contained 20·28 per cent. determined in successive portions, gave the following results, from which it is seen that the composition of the distillate was by no means so constant as that of the residue. An explanation of this fact will be given in the sequel:—

No.	1	2	3	4	5
Percentage of HCl in distillate	20·56	20·16	20·62	20·26	—
Ditto in residue . .	20·21	20·22	20·24	20·24	20.33

A fourth determination was made by distilling an acid containing 20·14 of HCl, and therefore weaker than the 16 atom hydrate, in three different portions, examining the composition of the residue in each case.

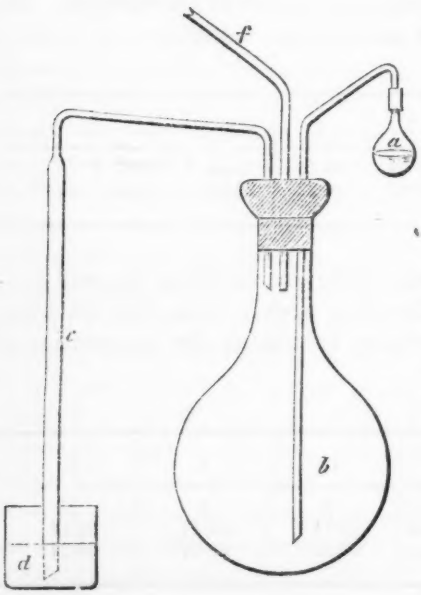
No.	1	2	3
Fraction of vol. after distillation	$\frac{5}{6}$	$\frac{3}{6}$	$\frac{1}{6}$
Per cent. of HCl before distillation	20·14	20·14	20·14
Ditto in residue after distillation	20·27	20·24	20·24

From the mean of these 10 experiments, we find that the residual aqueous hydrochloric acid, boiling at 110° C. under the ordinary atmospheric pressures, contains 20·25 per cent. of anhydrous hydrochloric acid. The calculated per centage composition of HCl + 16 HO being 20·22, we conclude, that, under pressures which differ but slightly from 0·760^{m}, the composition of the acid which has a constant boiling point, is that indicated by Bineau's formula.

In order now to determine whether the aqueous acid, having the composition HCl + 16HO, can be regarded as a definite chemical combination unalterable under change of physical conditions, we distilled this same acid under pressures varying considerably from that of the atmosphere, determining in each case the composition of the residue.

Experiments instituted for this purpose at pressures both greater and less than the barometric one, showed that, distilled under other pressures than 0·760^{m}, the 16-atom hydrate is decomposed, but that, for every pressure, an aqueous hydrochloric acid exists which, when distilled under that pressure, possesses a fixed composition and boiling point.

FIG. 6.



The distillation of aqueous hydrochloric acid under pressures less than 0·76^{m} was accomplished by connecting the flask containing the acid *a* (fig. 6) with a large bolthead of 20 litres capacity *b*, which could easily be rendered vacuous.

A divided barometric tube *c* (fig. 6) gave the pressure under which the distillation took place. As soon as the air had been removed from the apparatus to the extent required, the acid was heated to boiling, whilst the bolthead was kept cold by a stream of water. By occasionally opening a stop-cock on the tube *f* (fig. 6), con-

necting the apparatus with the vacuous cylinder of a large air pump, the mercury in the tube *c* could be kept within 5 mm. of the required height during the whole course of the distillation. The composition of the acids boiling under pressures greater than that of the atmosphere was obtained by distilling the liquid under a column of mercury of the required height. For every pressure, at least two experiments were made, one starting from a weaker and the other from a stronger acid than that found in the residue after distillation.

The following Table V contains the direct experimental results. Column I gives the number of the experiment; column II, the pressures, expressed in meters of mercury, under which the distillation was made; column III, the quantity of hydrochloric acid contained in 100 parts of the liquid before distillation; column IV, the quantity contained after distillation. The numbers marked* are those which correspond to definite hydrates, thus:

23·8 per cent. = HCl + 13HO. 22·5 = HCl + 14HO. 21·3 = HCl + 15HO. 20 22 = HCl + 16HO. 19·3 = HCl + 17HO. 18·4 = HCl + 18HO.

TABLE V.

I.	II.	III.	IV.	I.	II.	III.	IV.	I.	II.	III.	IV.
1	0·064	20·2*	23·3	12	0·38	21·7	21·3	23	0·765	20·20*	20·23*
2	0·065	23·8	22·9	13	0·38	21·6	21·5	24	0·768	20·20*	20·21*
3	0·100	21·3*	22½9	14	0·49	21·0	21·3	25	0·96	20· 2*	20· 0
4	0·100	23·8*	23·0	15	0·49	21·3*	21·4	26	1· 10	18· 0	19· 6
5	0·100	22·8	22·8	16	0·49	21·3*	20·9	27	1· 10	20· 2*	19· 6
6	0·210	21·3	22·2	17	0·63	20·2*	20·6	28	1· 77	18· 6	18· 5*
7	0·210	22·5*	22·2	18	0·63	20·2*	20·6	29	1· 77	19· 0	18· 5*
8	0·210	22·3	22·1	19	0·63	21·3*	20·6	30	2· 46	18· 0	18· 2
9	0·030	21·3*	21·7	20	0·63	21·3*	20·6	31	2· 51	18· 0	18· 1
10	0·030	23·8	22·0	21	0·63	20·7	20·6	32	2· 51	18. 0	18· 1
11	0·030	22·0	21·7	22	0·63	20·6	20·7	33	2· 51	18· 0	18· 0

From these direct observations the following interpolated values are obtained. The column marked P shows the pressure in metres of mercury, under which aqueous hydrochloric acid must be distilled to attain the constant composition given in the next column.

TABLE VI.

Pm	Per Centage of HCl.	Pm	Per Centage of HCl.	Pm	Per Centage of HCl.	Pm	Per Centage of HCl.
0·05	23·2	0·7	20·4	1·3	19·3	2·0	18·5
0·1	22·9	0·76	20·24	1·4	19·1	2·1	18·4
0·2	22·3	0·8	20·2	1·5	19·0	2·2	18·3
0·3	21·8	0·9	19·9	1·6	18·9	2·3	18·2
0·4	21·4	1·0	19 7	1·7	18·8	2·4	18·1
0·5	21·1	1·1	19·5	1·8	18·7	2·5	18·0
0·6	20·7	1·2	19·4	1·9	18·6		

Hence it is evident: (1) that there exists for each pressure a corresponding aqueous hydrochloric acid which undergoes no change in composition when distilled under this pressure, and therefore has a constant boiling point; (2) that the composition of these aqueous acids is different for each pressure, a gradual change in pressure being accompanied by a gradual alteration in the per-centage of hydrochloric acid. The relation between the composition of the acids of constant boiling points and the pressure under which they are distilled is represented by the curve, Fig. 7, in which the ordinates give the per-centage quantity of anhydrous acid, and the abscissæ the corresponding pressures. Having shown that the curve, Fig. 7, does not present any discontinuity, we must admit that the aqueous acid boiling without decomposition under the ordinary atmospheric pressure at 110° C., cannot be regarded as a true chemical hydrate, capable of existing within a certain altered range of physical conditions.

It next became necessary to determine whether the other acid of fixed composition described by Bineau, possesses a greater degree of stability than the one just examined. For this purpose we

shortened Bineau's process of preparation by passing a continuous current of dry air through aqueous acid contained in the burette-shaped vessel represented in Fig. 8. The tube *c* (Fig. 8) was attached to a suction-aspirator, and the dry air passed through the liquid from the tube *d*, a thermometer *b* giving the temperature of the experiment. An aqueous acid containing 20·2 p. c. of hydrochloric acid was placed in the apparatus (Fig. 8), and a current of dry air allowed to pass continuously through the liquid for some days at the ordinary atmospheric temperature (about 10°C.) At the expiration of this time, more than $\frac{2}{3}$ of the liquid had been volatilized, and the residue contained 23·3 p. c. of hydrochloric acid; after the air had passed through for some days longer, the residue contained 25·0 per cent.; on passing more air through this liquid, no further change of composition was effected, an analysis made two days later giving 24·9 per cent. This number, although not exactly agreeing with the theoretical result, HCl + 12HO which requires 25·2 p. c. of hydrochloric acid, corresponds sufficiently well to render Bineau's supposition of the existence of a 12-atom hydrate plausible enough. In order to determine whether the hypothetical hydrate preserves its composition under change of physical conditions, we determined the amount of hydrochloric acid contained in aqueous acids, through which a current of dry air had passed at different temperatures, until no further alteration in composition took place. The following Table (VII) gives the direct experimental results. Column I, shows the temperature of the liquid through which the air passed; II, the duration of the experiment in hours; III, the quantity of hydrochloric acid contained in 100 parts of the acid before the experiment; IV, the per-centage of HCl after the experiment.

Fig. 8.

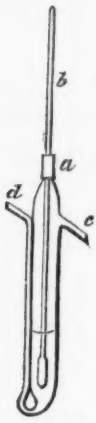


Table VII.

I.	II.	III.	IV.	I.	II.	III.	IV.	I.	II.	III.	IV.
0°	20	45·3	32·0	0°	6	25·0	25·0	30°	5	24·1	24·3
0°	10	32·0	28·9	10°	—	20·2	23·3	62°	5	22·8	22·9
0°	15	28·9	27·2	10°	48	23·3	25·0	77°	2	22·0	22·2
0°	6	27·2	26·4	10°	48	25·0	24·9	85°	1	21·7	21·7
0°	16	26·4	25·6	30°	4	23·8	24·4	91°	—	21·3	21·4
0°	20	25·6	24·8	30°	4	24·4	24·1	98°	—	21·1	21·1

At the higher temperatures, the current of air was allowed to pass through until about $\frac{3}{4}$ of the liquid had been volatilized. Table VIII, contains values interpolated from the direct experiments.

TABLE VIII.

t°	Per cents. of HCl.	Grms. of HCl. combined with 1 gr. of HO.	t°	Percents. of HCl.	Grms. of HCl. combined with 1 gr. of HO.	t°	Per cents. of H.Cl.	Grms. of HCl. combined with 1 gr. of HO.
0	25.0	0·333	40	23·8	0·312	80	22·0	0·283
5	24·9	0·331	45	23·6	0·308	85	21·7	0·278
10	24·7	0·328	50	23·4	0·305	90	21·4	0·273
15	24·6	0·326	55	23·2	0·302	95	21·1	0·267
20	24·4	0·323	60	23·0	0·298	100	20·7	0·261
25	24·3	0·320	65	22·8	0·295	110	20·24(?)	0·2538(?)
30	24·1	0·317	70	22·6	0·291			
35	23·9	0·315	75	22·3	0·286			

These experiments show that the aqueous acid approaching the composition HCl + 12HO possesses no higher claim to be considered as a true hydrate than HCl + 16 HO, a gradual alteration in the temperature at which the current of air passes, producing a corresponding gradual alteration in the composition of the acid.

A singular relation has been found to exist between the aqueous acids prepared by passing a current of dry air through the liquid at a constant temperature until no further change occurs, and those obtained by distillation under different pressures. It has been found that the composition of the aqueous acid prepared in these two different ways at the same temperature, has an identical composition; thus, for instance, an acid distilled under the pressure 0·38 meter boiling at a temperature of 91°C. contains 21·3 per cent. of hydrochloric acid, whilst any aqueous hydrochloric acid, heated with a current of dry air, under the common atmospheric pressure at 91°C. attains the constant composition of 21·4 per cent. of anhydrous acid. This is clearly seen in the annexed Table, in which Division I gives the pressures, boiling points and composition of the acids distilled under various pressures, found also in Table VI; and Division II the composition of the acids unalterable by passage of a current of dry air at the same temperatures.

TABLE IX.

I.			II.	
Pressure in meters.	Boiling point.	Contains p.c. of HCl.	Temp. C.	Contains p.c. of HCl.
0·10	61° to 62°	22·8	62°	22·9
0·21	76° to 77°	22·1	77°	22·2
0·30	84° to 85°	21·7	85°	21·7
0·38	91°	21·3	91°	21·4
0·49	97°	20·9	98	21·1
0·62	103°	20·6	—	—

From the foregoing experiments we may safely conclude that the supposition of the existence of hydrates of hydrochloric acid containing 12 and 16 atoms of water is unfounded. It is, however, remarkable that the boiling points of the acids of constant composition all lie about 9°C. higher than the boiling points of water under the same pressures. If then, we were to consider every aqueous acid as a mere mixture of water and liquid hydrochloric acid, the body thus produced must form a most remarkable exception to any relations at present known respecting the tensions of mixed vapours. We are, therefore, induced to admit the existence of certain attractions between the molecules of hydrochloric acid gas and water, which, if they do not give rise to definite chemical combinations, are at any rate essentially different from the attractions exerted between water and the other even the most soluble gases.

We may shortly explain the results of our experiments by supposing that certain definite chemical compounds of water and hydrochloric acid exist, but that they undergo a gradual alteration with variation of temperature, so that, for every temperature, a definite combination exists, which at this temperature remains unchanged by exposure to a current of dry air, and may be boiled without changing its composition, if the pressure is such that the liquid boils at this same temperature.* This explanation can, how-

* By this we do not mean to imply that the acid does not undergo decomposition upon distillation; on the contrary, we believe that the vapour of aqueous hydrochloric acid must be regarded as a mere mixture of anhydrous hydrochloric acid and steam: (1). Because Bineau showed that the vapour of the so-called 16-atom hydrate contained its constituents uncondensed; (2). From our own experiments, which prove that the composition of the distillate of this same acid is variable if the condensation is not complete.

ever, only be regarded as a mode of representing our results, which indeed, may be accounted for by many other suppositions, such, for instance, as the existence of other hydrates having definite atomic compositions.

B. Experiments with Ammonia.

I.—*Relation between the amount of Ammonia Absorbed in Water, at* 0° C. *and the Pressure under which the Absorption occurs.*

In a paper published in Liebig's "Annalen" in 1856, Carius details the results of a series of determinations of the solubility of ammonia in water at different temperatures and under the ordinary atmospheric pressure; he likewise gives experiments which would show that in mixtures of ammonia with other gases, the quantity of the former dissolved in water is strictly in accordance with Dalton's simple law. That a gas so soluble as ammonia in water should be absorbed in direct proportion to the pressure, appeared so remarkable, that we deemed it advisable to control these results by determinations made at 0° C. under direct pressures both greater and less than that of the atmosphere. For this purpose we, in the first place, determined the quantity of ammonia absorbed in water at 0° under the ordinary atmospheric pressures, employing exactly the same method that has been described under hydrochloric acid. Experiments thus made with every precaution gave, as the weight of ammonia absorbed by 1 grm. of water at 0° C. numbers differing widely from those obtained by Carius. In order to ascertain the cause of this discrepancy, we repeated the experiments precisely according to the method which he had adopted; but in this way we also obtained results which not only differed from those formerly found, but varied among themselves. As the result of a long critical investigation of both methods, we arrived at the conclusion that the plan adopted by Carius, viz., that of saturating with ammonia water contained in a tube open at top to the air, was liable to such considerable sources of error as to preclude its employment for exact measurements, whereas the method we have employed is free from such objections.

The chief causes of uncertainty in Carius' method were to be found in the facts:

I. That the time which elapses before the liquid attains a constant temperature is much longer than was imagined.

II. That the requisite absorptiometric equilibrium between the amount of dissolved gas and the temperature can never be brought about with certainty when water is saturated with ammonia in an open tube, owing to the rapid and irregular diffusive interchange continually going on between the dissolved ammonia and the atmospheric air above the liquid.*

III. That the numerical results are dependent upon a doubtful series of specific gravity determinations.

The following estimations of the solubility of ammonia in water at 0° C. under pressures varying from 0·018 to 1·96 meters of mercury, were made according to the methods already described. The total quantity of ammonia contained in the bulb-vessel was determined by first supersaturating with a standard hydrochloric acid, the strength of which was exactly ascertained by analysis with pure silver, and then adding a standard soda-solution until the point of alkalinity was reached.

Only in the experiments made under pressures greater than that of the atmosphere, did we adopt a plan slightly different from the foregoing. In these cases, we saturated water, contained in the bulb-apparatus (fig. 1), with ammonia at a temperature of

* The following experiment, as being one out of a number, may be cited in proof of the above assertion. About 10 grms. of water was placed in an open tube of the dimensions used by Carius, and through this ammonia was passed, the whole being plunged in a bath of melting ice. At the commencement of the experiment, a thermometer, placed at the bottom of the liquid, showed a temperature of + 20° C; as soon as the evolution of gas had continued for 15 minutes, the ammonia began to pass through unabsorbed, and the temperature sank to + 6°; after the gas had passed through for 15′ longer (the extent of time allowed by Carius), the temperature was still + 4°·8; 12 minutes later, the temperature had sunk to + 0°·7, and after 13 minutes more to + 0°·5. The gas now passed somewhat more slowly through the liquid, and at 10 minutes after the last observation, the thermometer showed a temperature of — 0°·2, which, five minutes later, diminished to — 0°·8, and at the moment of the stoppage of the current of gas, the mean temperature of the liquid sank to — 1°·2. The temperature of the liquid at the surface exposed to the air was, however, much lower, the thermometer when placed at the surface showing a temperature of — 3°·2 even when a rapid current of gas passed through the liquid. So great, indeed, is the absorption of heat in this change of ammonia from solution to the gaseous state, that we have easily succeeded in freezing about 20 grms. of mercury by passing a rapid current of air through a few cubic-centimeters of water saturated with ammonia, at — 10° C.

−30°C under the atmospheric pressure, then sealed one limb of the apparatus, whilst the other remained connected by an air-tight joint to the manometer *d* (fig. 5). The bulb was now gradually allowed to attain the temperature of 0°, and when all evolution of gas had ceased, and the height of the column of mercury in the tube remained perfectly constant, the apparatus was closed in the usual manner, and the ammonia determined by analysis.

The following Table X. contains the direct results of experiments made at 0° C. under different pressures. P signifies the partial pressure of the gas in metres of mercury; G the weight in grammes of ammonia absorbed under the circumstances of the experiment by 1 grm. of water. Experiments 1 to 7 were made under pressures lower than one atmosphere; experiments 16 to 23 under pressures greater than an atmosphere; the remaining experiments, Nos. 8 to 15, under common atmospheric pressure. A graphic representation of all the results enabled us to reduce the latter experiments to 0·76^{m} and the numbers thus obtained are also found in the table. From these numbers an idea of the trustworthiness of the method may be obtained. We find that the maximum deviation from the mean result is 877+10 and −14, whilst the mean deviation is + 6, or 0·7 per cent. of the whole.

TABLE X.

No.	P.	G.	No.	P.	G.	G. reduced to 0 ·76m.	No.	P.	G.
1	0·018	0·074	8	0·753	0·870	0·875	16	0·904	0·955
2	0·097	0·274	9	0·759	0·869	0·869	17	0·912	0·994
3	0·241	0·463	10	0·759	0·882	0·883	18	1·261	1·292
4	0·268	0·478	11	0·761	0·877	0·876	19	1·264	1·268
5	0·452	0·652	12	0·762	0·864	0·863	20	1·266	1·248
6	0·707	0·845	13	0·763	0·889	0·887	21	1·281	1·290
7	0·712	0·855	14	0·763	0·878	0·876	22	1·960	2.134
			15	0·769	0·891	0·885	23	1·963	2·137

From the direct observations the annexed interpolated values are obtained. In Table XI. P again signifies the partial pressure of the gas, and G the weight of ammonia absorbed in 1 grm. of water at 0°C.

TABLE XI.

P.	G.	P.	G.	P.	G.	P.	G.
0·00	0·000	0·25	0·465	0·85	0·937	1·45	1·469
0·01	0·044	0·30	0·515	0·90	0·968	1·50	1·526
0·02	0·084	0·35	0·561	0·95	1·001	1·55	1·584
0·03	0·120	0·40	0·607	1·00	1·037	1·60	1·645
0·04	0·149	0·45	0·646	1·05	1·075	1·65	1·707
0·05	0·175	0·50	0·690	1·10	1·117	1·70	1·770
0·75	0·228	0·55	0·731	1·15	1·161	1·75	1·825
0·100	0·275	0·60	0·768	1·20	1·208	1·80	1·906
0·125	0·315	0·65	0·804	1·25	1·258	1·85	1·976
0·150	0·351	0·70	0·840	1·30	1·310	1·90	2·046
0·175	0·382	0·75	0·872	1·35	1·361	1·95	2·120
0.200	0·411	0·80	0·906	1·40	1·415	2·00	2.195

The graphic representation of the relation between absorbed gas and pressure is well seen by reference to the curve NH_3, fig. 4.

From this curve, as well as from the foregoing numbers, it is evident (1) that the quantity of ammonia absorbed by water at 0° C. is far from being proportional to the pressure; and (2) that for equal increments of pressure up to about 1 metre of mercury, the corresponding increments of absorbed ammonia continually diminish, but that above this point the amount of dissolved gas increases in a more rapid ratio than the pressure. A comparison between the curve and the straight line *b*, cutting it at the point corresponding to the pressure $0{\cdot}76^m$, and passing through the origin, shows clearly the great difference which exists between the simple law of Henry and the law regulating the absorption of ammonia in water at 0° under different pressures.

I.—*Relation between the amount of ammonia absorbed in water under the ordinary atmospheric pressures, and the temperature at which the absorption occurs.*

The experiments made with ammonia at different temperatures were conducted exactly according to the method described under hydrochloric acid. The following were the results obtained. Column I contains the observed barometric pressures; column II, the temperatures; column III, the weight in grms. of ammonia absorbed by one grm. of water.

TABLE XII.

No.	I.	II.	III.
1	0·760 m.	0°0 C.	0·875 grm.
2	0·766	6°2	0·756
3	0·749	6°9	0·723
4	0·749	6°9	0·726
5	0·742	15°4	0·586
6	0·755	15°4	0·589
7	0·744	24°1	0·465
8	0·751	24°1	0·471
9	0·768	35°3	0·350
10	0·760	35°3	0·354
11	0·768	54°2	0·202

As the influence of pressure on the amount of absorbed gas is, in the case of ammonia, very considerable, it was impossible to reduce these results to a constant partial pressure. We therefore give the following values interpolated under the supposition that all the experiments were made under pressure of $0{\cdot}76^{m}$, only as an approximation to the truth. Column I. of the annexed Table contains the temperatures; column II. the corresponding weight of ammonia absorbed by one gramme of water.

TABLE XIII.

I.	II.	I.	II.	I.	II.	I.	II.
0°C.	0·875	16°C.	0·582	32°C.	0·382	48°C.	0·244
2°	0·833	18°	0·554	34°	0·362	50°	0·229
4°	0·792	20°	0·526	36°	0·343	52°	0·214
6°	0·751	22°	0·499	38°	0·324	54°	0·200
8°	0·713	24°	0·474	40°	0·307	56°	0·186
10°	0·679	26°	0·449	42°	0·290		
12°	0·645	28°	0·426	44°	0·275		
14°	0·612	30°	0·403	46°	0·259		

These numbers and the curve *b*, (fig. 5,) show that the amount of absorbed ammonia varies much more considerably with change of temperature than is the case with hydrochloric acid.

XVI.—*On Bases produced by Nitrous Substitution.*

By C. S. Wood.

In his remarkable memoir* on the action of reducing agents on nitro-compounds, in which he first pointed out the formation of organic bases by the substitution of hydrogen for oxygen, Zinin has recorded some experiments on the deportment of dinitronaphtaline [nitronaphtalese] with sulphuretted hydrogen. He states that this action gave rise to the formation of a basic compound, crystallizing in delicate copper-red needles, and yielding, with acids, white scaly salts.

In a subsequent paper† Zinin returns to the action of sulphuretted hydrogen upon dinitronaphtaline, and gives a fuller account of the products obtained in this process. He states that the base thus produced crystallizes in colourless needles of great brilliancy which contain $C_{10}H_5N$ or $C_{20}H_{10}N_2$. This body possesses well-defined basic properties, and is described under the name *seminaphtalidam*.

From this latter communication it would appear that the copper-red coloration originally observed was due to the presence of a foreign colouring matter, which can be separated by crystallizing the base alternately from water and alcohol.

Subsequently, the same body appears to have been observed by Laurent,‡ who states that the action of sulphuretted hydrogen upon dinitronaphtaline gives rise to the formation of a carmine-red alkali. He did not, however, analyse this substance, and the discovery of nitraniline§ having established the existence of basic nitro-substitutes, the compound in question has hitherto been considered to be nitronaphtylamine.

At the suggestion of Dr. Hofmann, I was led to examine this body, and as my results do not agree with the above supposition, I beg to lay them before the Chemical Society.

To prepare the red base, a quantity of dinitronaphthaline is introduced into a flask, together with some weak alcoholic ammonia; the latter should be sufficient in quantity nearly to dissolve the dinitronaphthaline. It is then heated to the boiling point, and a

* Bulletin Scientifique de St. Petersbourg, x, 18. † J. pr. Chem. xxxiii, 29.

‡ Compt. rend. xxxi. 538. § Muspratt and Hofmann, Mem. Chem. Soc. vol. iii.

stream of sulphuretted hydrogen passed through it for some hours, or until the spirit has nearly distilled off. Sulphuric acid is then added until the solution has an acid reaction; it is then boiled and rapidly filtered while hot. The filtrate, on cooling, deposits a quantity of crystals of the sulphate, which may be purified by a few crystallizations from boiling water. The addition of ammonia to the solid salt immediately decomposes it, changing the colour to a fine dark carmine-red.

The base thus liberated is washed with cold water to free it from ammonia, and finally purified by recrystallization from water, or very dilute spirit.

Thus prepared, the substance, for which I propose the provisional name *Ninaphtylamine*, is a light flocculent mass, composed of beautiful little acicular crystals, which are partially decomposed by exposure to a temperature of 100°C. It is extremely soluble in alcohol and ether; insoluble in cold water; soluble, although with difficulty, in boiling water.

For combustion, the substance was dried *in vacuo* over sulphuric acid.

I. 0·21 grm. of the base gave—

0·5375 grm. of carbonic acid, and
0·0950 grm. of water.

The percentage composition thus given is—

Carbon	69·76
Hydrogen	5·02

A second combustion gave similar results.

II. 0·28955 grm. of the base gave—

0·7405 grm. of carbonic acid, and
0·127 grm. of water.

The percentage composition being—

Carbon	69·72
Hydrogen	4·87

III. A determination of the nitrogen was also made by the process of Dumas; in this case also the substance was dried over sulphuric acid *in vacuo*.

0·4700 grm. of the base gave—

67·0 cubic centimeters of nitrogen gas,

the barometric pressure being 0·7714m. and the temperature of the water 12°C.

These results lead to the following expression :

$$C_{20}H_8N_2O_2.$$

		Theory.	Experiment.			Mean.
			I.	II.	III.	
20 equivs. of Carbon	120	69·77	69·76	69·72	..	69·74
8 „ Hydrogen	8	4·65	5·02	4·87	..	4·945
2 „ Nitrogen	28	16 28	..	..	17·22	17·22
2 „ Oxygen	16	9·30	..	..	..	..
1 „ Ninaphtylamine	172	100·00				

This formula, which I propose, has been confirmed by the examination of several of the salts of the new base.

Sulphate of Ninaphtylamine is obtained, either by recrystallizing the crude salt formed in the preparation of the body, or by dissolving the base in dilute sulphuric acid. It forms white scaly crystals, which are decomposed by repeated crystallization from pure water. It is also partially decomposed by exposure to 100°C. The salt dried *in vacuo* over sulphuric acid gave the following numbers—

0·20275 grm. decomposed by chloride of barium gave—

0·10800 grm. of sulphate of barium.

The formula $2C_{20}H_8N_2O_2.H_2S_2O_8$ requires the following values—

		Theory.	Experiment.
2 equivs. of Ninaphtylamine	344	77·83	77·7
1 „ Hydrated sulphuric acid	98	22·17	22·3
1 „ Hydrosulphate	442	100·00	100·0

Hydrochlorate of Ninaphtylamine.—When the base is dissolved in hydrochloric acid, a fine white salt is produced, which crystallizes in needles. It is easily decomposed by water, and by exposure to 100°C.

0·1752 grm. of the base, decomposed by nitrate of silver, gave—
0·1200 grm. of chloride of silver.

This result agrees with the formula—

$$C_{20}H_8N_2O_2.HCl.$$

		Theory.	Experiment.
1 equiv. of Ninaphtylamine	172·0	82·49	82·63
1 „ Hydrochloric acid	36·5	17·51	17·40
	208·5	100·00	100·03

The *platinum-salt of Ninaphtylamine* forms rather soluble yellowish brown crystals, which may be dried at 100°C. without decomposition. It is best prepared by adding a concentrated solution of bichloride of platinum to an alcoholic or etherial solution of the base also concentrated. It has the usual constitution containing:

$$C_{20}H_8N_2O_2.HCl.PtCl_2,$$

as will be shown by the following numbers—

I. 0·405 grm. of the salt gave, on combustion—
0·471 grm. of carbonic acid, and
0·099 grm. of water.

II. 0·168 grm. of the salt gave, on ignition—
0·0437 grm. of platinum.

		Theory.	Experiment.	
			I.	II.
20 equivs. of Carbon	120	31·73	31·7	..
9 „ Hydrogen	9	2·38	2·72	..
2 „ Nitrogen	28	7·40	..	..
2 „ Oxygen	16	4·23	..	..
3 „ Chlorine	106·5	28·16	..	..
1 „ Platinum	98·7	26·10	..	26·01
1 „ Platinum-salt	378·2	100·00		

If it be permitted, in the absence of further experimental evidence, to speculate on the molecular constitution of the body which forms the subject of this paper, the simplest interpretation of its formation and composition would be to view it as a substitution-product of naphtylamine, in which hydrogen is replaced by binoxide of nitrogen, thus differing from ordinary nitro-sub-

stitutes, which are assumed to contain the tetroxide of nitrogen; thus—

Naphtylamine $C_{20}H_9N = \left.\begin{matrix} C_{20}H_7 \\ H \\ H \end{matrix}\right\} N$

Ninaphtylamine $C_{20}H_8N_2O_2 = \left.\begin{matrix} C_{20}[H_6NO_2] \\ H \\ H \end{matrix}\right\} N$

Its formation would then be represented by the equation—

$$\underbrace{C_{20}[H_6(NO_4)_2]}_{\text{Dinitronaphtaline.}} + 8HS = 6HO + 8S + \underbrace{C_{20}H_8(NO_2)N}_{\text{Ninaphtylamine.}}$$

Bodies in which binoxide of nitrogen figures as a material of substitution are as yet extremely rare, whilst nitro-substitutes containing the elements of hyponitric acid are of the most general occurrence.

Some chemists have considered nitrous ether as a binoxide of nitrogen derivative of alcohol; thus—

Alcohol . . . $C_4H_6O_2$

Nitrous ether . . $C_4 \left\{\begin{matrix} H_5 \\ NO_2 \end{matrix}\right\} O_2$

The most interesting illustrations of this kind of substitution, however, have been furnished by Messrs. Perkin & Church* in the colouring matters produced by the action of nascent hydrogen on dinitro-substitutes, or of nitrous acid on certain monamines.

Phenylamine . . . $C_{12}H_7N$

Nitrophenyline . . . $C_{12}\left(\begin{matrix} H_6 \\ NO_2 \end{matrix}\right)N$

Naphtylamine . . . $C_{20}H_9N$

Nitrosonaphtyline . . $C_{20}\left(\begin{matrix} H_8 \\ NO_2 \end{matrix}\right)N$

Expressed by these formulæ, these substances appear to be very closely allied to the basic body which I am describing. In fact,

* Chem. Soc. Qu. J. ix. 1.

nitrosonaphtyline has the same composition as ninaphtylamine; but even a superficial comparison of the properties of the two bodies excludes any idea of their identity. It deserves to be noticed that the formulæ of the colouring matters in question have not as yet been finally established by the analysis of any compounds; they appear, like colouring matters in general, to be of an indifferent character. It is not improbable that these coloured derivatives may be formed by the association of several molecules, and this idea receives some support from the discovery of ninaphtylamine.

The formation of this body promises to add considerably to the number of the nitro-substitutes of the aromatic monamines. To each of these probably corresponds a nitrous and a nitric substitution base; but as yet we are unacquainted with a single one in which both derivatives are known, as shown by a glance at the groups best known.

Phenyl Group.

Phenylamine [aniline] . .	$\left.\begin{matrix} C_{12}H_5 \\ H \\ H \end{matrix}\right\} N$
Unknown . . .	$\left.\begin{matrix} C_{12}[H_4NO_2] \\ H \\ H \end{matrix}\right\} N$
Nitrophenylamine . .	$\left.\begin{matrix} C_{12}(H_4NO_4) \\ H \\ H \end{matrix}\right\} N$

Naphtyl Group.

Naphtylamine . .	$\left.\begin{matrix} C_{20}H_7 \\ H \\ H \end{matrix}\right\} N$
Ninaphtylamine . .	$\left.\begin{matrix} C_{20}(H_6NO_2) \\ H \\ H \end{matrix}\right\} N$
Unknown . . .	$\left.\begin{matrix} C_{20}(H_6NO_4) \\ H \\ H \end{matrix}\right\} N$

The experiments just described were performed in Dr. Hofmann's laboratory, and I take this opportunity of thanking him for his kind advice throughout the investigation.

XVII.—*On the action of Hydrochloric Acid upon Sulphide of Mercury, in the presence of certain other substances.*

By Frederic Field.

In my late memoir upon the mineral "ammiolite," a method was described for the separation of mercury and antimony, by heating the sulphides of those metals in hydrochloric acid. The experiments were tried upon the tersulphide of antimony, and answered extremely well, as only moderately strong hydrochloric acid was employed, and the liquid subjected to a heat below ebullition. When pentasulphide of antimony is present, sulphur is eliminated, and a solution of terchloride is formed:

$$SbS_5 + 3HCl = SbCl_3 + 3HS + 2S.$$

The mercurial sulphide is consequently mixed with free sulphur, which renders an estimation of that element imperative, in order to arrive at the amount of mercury.

The difference of opinion which arose between Domeyko and myself, regarding the state in which the antimony existed in ammiolite, led to a somewhat lengthened discussion upon the nature of that mineral, he affirming that it was as antimonic acid, while my own conviction was in favour of teroxide. As the investigation of ammiolite had occupied both of us for many months, the mineral assumed, for us at least, an interest which it probably would scarcely have claimed for those not engaged in its research; but one or two facts have been elicited during the analysis, which are somewhat interesting and important, and have not been, as far as I am aware, recognized in chemical science. On boiling ammiolite with hydrochloric acid, nearly all the antimony, and much of the mercury is dissolved; and upon the addition of iodide of potassium in excess to the solution, the precipitated iodide of mercury is redissolved, and the liquid remains nearly colourless. From this it was inferred, that the antimony existed entirely as teroxide, inasmuch as the higher oxides of that metal, when in solution in hydrochloric acid, eliminate free iodine upon the addition of iodide of potassium. Bunsen, in a recent paper, recommends this test for the degree of oxidation of antimony when in solution. M. Domeyko mentioned to me, that on boiling sul-

phide of mercury with antimonic acid in strong hydrochloric acid, the whole of the sulphide was dissolved, and a yellowish white powder remained, which he believed consisted principally of subchloride of mercury (calomel). As hydrochloric acid has very little action upon sulphide of mercury unless highly concentrated and at a boiling temperature, it occurred to me that it would be interesting to examine how far this acid influenced the solubility of the sulphide, not only when in conjunction with antimony, but also with other bodies, that might probably be associated with it in the mineral world.

Antimonic Acid.—When antimonic acid and sulphide of mercury are boiled together in hydrochloric acid, rapid decomposition takes place after a few minutes. Vermilion, for instance, speedily loses its colour; a clear solution is formed with a small deposit of sulphur, and the antimonic acid is reduced.

The reduction of the antimonic acid is more apparent when a large excess of sulphide of mercury is present. The reaction is probably more complicated, as there is a slight evolution of sulphuretted hydrogen during the ebullition.

A solution of terchloride of antimony in strong hydrochloric acid does not act upon sulphide of mercury.

Arsenic Acid.—When arsenic acid is boiled with sulphide of mercury in hydrochloric acid, the decomposition is very rapid. The residue is yellow, consisting entirely of sulphur, which, after continued boiling, separates in clear yellow globules. It is rather more difficult to understand the reaction in this case, as the arsenic acid does not seem, in any great measure, to be reduced. On filtering the liquid from the sulphur and evaporating, rather large crystals are formed of chloride of mercury, and on evaporation to dryness, the residue instantly redissolves in water. On addition of ammonia to the solution, a white precipitate is produced, and from the filtrate sulphate of magnesia gives immediately a crystalline precipitate of ammonia-magnesian arseniate. Indeed, although the sulphide of mercury was sometimes used in considerable excess, little, if any, arsenious acid could be detected.

Sesquichloride of Iron, with excess of hydrochloric acid, when boiled with sulphide of mercury, is reduced after ebullition for a few hours, much sulphur being deposited.

Protochloride of Copper is very quickly decomposed; sulphur is eliminated, and the liquid assumes a dark brown colour, indica-

tive of the solution of subchloride of copper in hydrochloric acid. After evaporation water precipitates a crystalline white powder, which consists entirely of subchloride of copper.

Peroxide of Manganese.—When peroxide of manganese is boiled with hydrochloric acid and sulphide of mercury, the latter is instantly decomposed, with separation of sulphur. When the sulphide is in excess, no chlorine is evolved.*

$$MnO_2 + 2HCl + HgS = MnCl + HgCl + S + 2HO$$

Sesquichloride of Chromium in strong hydrochoric acid, exerts no action upon sulphide of mercury, even after long boiling.

Sesquichloride of Uranium, under similar circumstances, produces no effect.

The above reactions tend to prove, that where certain substances are associated with antimonial compounds, the degree of the oxidation cannot be determined after its solution in hydrochloric acid. Although I still am of opinion, from various reasons, that the metal exists as teroxide in the mineral, the non-disengagement of free iodine on addition of iodide of potassium, cannot be considered as by any means conclusive.

XVIII.—*On the action of Boracic Acid upon the Salts of the more Volatile Acids at high temperatures.*

By A. Norman Tate,

STUDENT IN THE LIVERPOOL COLLEGE OF CHEMISTRY.

It is stated in most of the Chemical works of note, that boracic acid expels the more volatile acids from their salts at high temperatures.

* Von Kobell has shown that when metallic iron is heated with binoxide of manganese and hydrochloric acid, no chlorine is evolved, and the difficultly soluble binoxide is entirely decomposed. I have found that the same reaction takes place with metallic copper. When the finely-divided metal is treated with hydrochloric acid, and binoxide of manganese added, the metal is immediately dissolved, no evolution of chlorine takes place, and a very rapid solution is effected, a small residue of silica (from the native manganese ore), alone remaining. Should, therefore, either iron or copper be introduced into oxide of manganese, it would be impossible to estimate the amount of MnO_2 by the quantity of chlorine evolved.

In the English translation of Gmelin's Chemistry, the following passage occurs: "At a red heat, boracic acid expels all acids which are more volatile than itself."

Brande says: "The affinity of boracic acid for bases in the humid way is feeble, little exceeding that of carbonic acid; but at a red heat, it displaces all the more volatile acids."

Professor Graham observes: "At a red heat this acid (boracic acid) decomposes even the sulphates, from its comparative fixity."

Sir Robert Kane, in his Elements of Chemistry, states: "If a mixture of sulphate of soda and boracic acid be heated to redness in a crucible, the sulphuric acid will be driven off in consequence of its volatility, whilst the fixed boracic acid will remain combined with *the whole quantity of the base*."

I give in the following pages the results of some experiments of my own on this subject, which, however, contradict in a certain degree the foregoing statements, especially the last.

The boracic acid used in all the following experiments was perfectly anhydrous, and carefully prepared by myself for the purpose.

Action upon the Sulphates.—The sulphates of potassa and soda were chosen for most of these experiments, on account of their stability.

Experiment 1.—I mixed 0·435 grm. of sulphate of potassa = 0·20 grm. of sulphuric acid (SO_3), and 0·175 grm. of anhydrous boracic acid, which is in the proportion of one equivalent of each; placed the mixture in a platinum crucible, protected in the usual way, and heated for some time in a charcoal fire. The crucibles were then removed, and subjected to the heat of a blacksmith's furnace for about twenty minutes. The fused mass was then taken from the crucible, dissolved in water, the solution acidulated with nitric acid, and chloride of barium added to precipitate the sulphuric acid remaining. There was obtained 0·410 grm. of sulphate of baryta = 0·140 of sulphuric acid, showing a loss of not more than 0·060 grm. of that substance.

Exp. 2.—A mixture of 0·355 grm. of sulphate of soda = 0·200 grm. of sulphuric acid, and 0·35 grm. of boracic acid, or in the proportion of one equivalent of the former to two of the latter, was treated in the same manner as mixture 1.

$BaO.SO_3$ obtained, 0·440, grm. = 0·150 grm. of SO_3 = 0·05 grm. loss of SO_3.

The following mixtures were heated in a charcoal fire, and

kept in a state of fusion, at a very strong red heat, until they ceased to lose weight, the time varying from an hour and a-half to two hours and a-quarter. The fused mass was afterwards dissolved in water, and the sulphuric acid remaining was determined as sulphate of baryta in the usual manner.

Exp. 3.—0·870 grm. of sulphate of potassa = 0·400 grm. of sulphuric acid, and 0·350 grm. of boracic acid, or one equivalent of each.

Sulphate of baryta obtained 0·959 grm. = 0·328 grm. of sulphuric acid = 0·072 grm. loss of sulphuric acid.

Exp. 4.—0·71 grm. of sulphate of soda = 0·40 grm. of sulphuric acid, and 0·35 grm. of boracic acid, or 1 equiv. of each. Sulphate of baryta obtained 0·967 grm. = 0·33 grm. of sulphuric acid = 0·07 grm. loss of sulphuric acid.

Exp. 5.—0·71 grm. of sulphate of soda = 0·40 grm. of sulphuric acid, and 0·70 grm. of boracic acid, or 1 equiv. of the former to 2 equiv. of the latter.

$BaO.SO_3$ obtained 0·909 grm. = 0·31 of SO_3 = 0·09 grm. loss of SO_3.

Exp. 6.—0·71 grm. of sulphate of soda, or 1 equiv., and 1·40 grms. of boracic acid, or 4 equiv. $BaO\,SO_3$ obtained 0·688 grm. = 0·236 grm. of SO_3 = 0·164 grm. loss of SO_3.

Exp. 7.—0·71 grm. of sulphate of soda, and 3·50 grms. of boracic acid, or 1 equiv. of the former to 10 equiv. of the latter. $BaO{\cdot}SO_3$ obtained 0·379 grm. = 0·13 grm. of SO_3 = 0·27 loss of SO_3. Thinking that, perhaps, if the two substances were still more intimately mixed, all the sulphuric acid might be expelled, I dissolved them in water:

Exp. 8.—0·71 grm. of sulphate of soda (1 equiv.) and 0·40 grm. of boracic acid (rather more than 1 equiv. to allow for any loss during evaporation) were dissolved and evaporated to dryness, and the residue was fused, keeping it a strong red heat until it ceased to lose weight. Subsequent estimation of sulphuric acid yielded 0·972 grm. of BaO,SO_3 = 0·333 grm. of SO_3 = 0·67 grm. loss of SO_3.

Exp. 9.—A mixture of 1·42 grms. of sulphate of soda, and 0·35 grm. of boracic acid, or 2 equiv. of the sulphate and 1 equiv. of the acid, was treated as mixtures 3 to 7. BaO,SO_3 obtained 2·13 grms = 0·730 grm. of SO_3 = 0·07 grm. loss of SO_3.

Exp. 10.—I next experimented upon a mixture of sulphate of soda and perfectly anhydrous biborate of soda, 0·71 grm. (1 equiv.) of the former, and 2·02 (2 equiv.) of the latter. After

being heated, and kept in a state of fusion for half an hour, it was found not to have lost weight. The two substances were thoroughly mixed after fusion, and not separated as in the other mixtures. The addition of 0·35 grm. of boracic acid, and subsequent fusion, produced however a separation of the substances into two layers, and a very slight loss of SO_3.

Exp. 11.—I next fused a mixture of anhydrous sulphate of magnesia and boracic acid, having the latter in large excess. All the sulphuric acid was not expelled, there being sufficient left to produce a copious precipitate of sulphate of baryta upon addition of chloride of barium to the acidified solution. I did not try this experiment quantitatively,

Exp. 12.—Was made with a mixture of sulphate of baryta and boracic acid in equivalent proportions, viz., 1·166 grms. of the former and 0·35 grm. of the latter. There remained, after heating, 0·814 grm. of $BaO.SO_3$ = 0·279 grm. of SO_3 = 0·121 grm. loss of SO_3.

In all the foregoing experiments, with the exception of the last, and the mixture of sulphate and biborate of soda, the two substances, however intimately mixed previously, even when dissolved and afterwards evaporated to dryness, as in No. 9, separated during fusion into two layers, owing to their being of different densities when in that state. I endeavoured to produce combination by stirring, but was unable to do so. Upon cooling, the sulphate appeared as a white crystalline mass at the bottom of the crucible, whilst the boracic acid appeared as a colourless transparent glass, above the sulphate. This clear glass, however, when carefully separated from the white mass of sulphate, dissolved in water, and the solution acidified with nitric acid, yielded upon addition of chloride of barium, a rather copious precipitate of sulphate of baryta, showing that some, at any rate, of the sulphate had been thoroughly mixed with the boracic acid, without losing its acid.

From a review of the above experiments, it will be seen that boracic acid does expel some of the acid from sulphates at high temperatures, but not at all in equivalent proportions, as would be inferred from the statements before given; nor is the amount driven off in any relative proportion. Neither does it appear to make any difference what quantity of sulphate is present.

The following table shows the quantity of sulphuric acid driven off by the boracic acid in the various experiments, in proportion to the weight of the latter used:—

No. 1	. .	17·14 per cent.
„ 2	. .	14·28 „
„ 3	. .	20·57 „
„ 4	. .	20·00 „
„ 5	. .	12·85 „
„ 6	. .	11·71 „
„ 7	. .	7·71 „
„ 8	. .	19·14 „
„ 9	. .	20·00 „
„ 12	. .	34·57 „

The fact that the two substances separate when in a state of fusion would rather lead us to think that the obstacles to the expulsion of the whole quantity of sulphuric acid are partly mechanical; for it would naturally be expected, that if boracic acid expels some sulphuric acid, it would expel it equivalent for equivalent; and it also appears strange that it should eliminate a larger quantity from sulphate of baryta than from sulphate of soda. But then again, the circumstance of the clear glass containing sulphuric acid, which must have been thoroughly mixed with the boracic acid, and therefore, have offered no mechanical obstacle to its expulsion, would favour the belief that sulphuric acid has, even at a strong red heat, a more powerful affinity for the base than boracic acid has. This belief is also strengthened by the results of experiment 11; for certainly if a base, like magnesia, gives off a portion of its acid when heated alone, it may be expected that when another acid like boracic acid is present, as we may term it a predisposing cause, all the sulphuric acid would be expelled.

When, however, the sulphates of zinc and nickel, and one or two similar sulphates, are fused with boracic acid, all the sulphuric acid is expelled, and a borate of zinc, &c., remains. This cannot, however, be taken as a proof that the acid is driven off by the boracic acid, for these sulphates are decomposed when heated alone, all, or very nearly all, the acid being evolved.

Action upon Chlorides.—In order to try the action of boracic acid upon chlorides at high temperatures, I fused together chloride of sodium and chloride of potassium with that acid. In both cases, the same separation took place as in the case of the sulphates, and a portion of the chloride volatilized unaltered. The two substances were also dissolved in water, the solution evaporated to dryness, and the residue fused. Here also a separation took place,

and the chloride volatilized unaltered, as in the other experiments.

I afterwards fused together mixtures of boracic acid and chloride of barium, and chloride of calcium. These substances also separated when fused. These mixtures were heated for several hours without driving off the chlorine, but there was a gradual loss of that element. After exposure to a strong red heat for nearly six hours, 0·100 grm. was lost from a mixture containing 1·04 grms. of chloride of barium, and from a mixture containing 0·755 grm of chloride of calcium, 0·08 grm.

Action upon Iodides and Bromides.—When a mixture of boracic acid and iodide of potassium was heated to redness, a similar result ensued as when chloride of potassium was used, viz., a separation of the two substances and partial volatilization of the iodide. Slight traces of iodine vapours were however perceptible.

With bromide of potassium no vapours of bromine, *or any decomposition whatever*, were discernible.

Action upon Nitrates and Carbonates.—Both nitric and carbonic acids are *completely expelled* from their salts by boracic acid at a red heat, as is generally understood.

From these experiments it appears, then, that the statements given at the commencement of this paper are incorrect; for certainly we are led to infer, that boracic acid expels *the whole* of the more volatile acids from their salts at a red heat, which is decidedly not the case.

In conclusion, I would remark that these experiments, many of them suggested by Dr. Muspratt, whose advice during the investigation greatly assisted me, have been repeated several times, in order to test their accuracy.

I intend shortly to investigate the action of silicic and phosphoric acids upon the salts of other acids at high temperatures.

ANNIVERSARY MEETING
OF THE CHEMICAL SOCIETY.

March 30, 1859.

Dr. MILLER, Vice-President, in the Chair.

The following Report was read by the Secretary:

REPORT OF THE PRESIDENT AND COUNCIL.

THE Council have much pleasure in congratulating the Fellows upon the prosperous condition of the Society. During the past year the meetings have taken place regularly at Burlington House, on the first and third Thursdays in the month; and, judging from the large attendances, the Council, after two years experience, have every reason to be satisfied with the change of locality and day of meeting, whereby the Fellows of the Chemical Society are brought into association with those of the Royal and Linnæan Societies.

During the past year, the Chemical Society has increased the number of its Fellows from 277 to 302, as shewn in the following statement:

Number of Fellows at last Anniversary, March 30, 1858		277
Fellows since admitted	34	
Fellows deceased	3	
Fellows removed in default of subscription	6	
Increase		25
Present number of Fellows		302
Foreign Members		24
Associates		9

At the last Anniversary the number of Associates was thirteen. Of these, three have since been elected Fellows, and five have ceased to be Associates in consequence of the time for which they were elected having expired. Four fresh elections have been made, so that the present number of Associates is nine.

The names of the deceased Fellows are Hugh Lee Pattinson, F.R.S., Newcastle-on-Tyne; Thornton John Herapath, Bristol; William Gregory, M.D., F.R.S.E., Edinburgh.

Mr. Pattinson was one of the original Members of the Chemical Society.

The following Papers, twenty-four in number, have been read at the Meetings of the Chemical Society, between March 30, 1858, and March 30, 1859.

1. "On a New Method of preparing Propionic Acid:" by Mr. J. A. Wanklyn.
2. "On some Compounds of Iodide and Bromide of Mercury with the Alkaloids:" by Mr. T. B. Groves.
3. "On the Quantitative Estimation of Sulphides, Sulphites, Hyposulphites, and Sulphates, in the presence of one another:" by Mr. J. W. Kynaston.
4. "On Nitrate of Amyl and its Derivatives." by Dr. F. Guthrie.
5. "On a New Method of preparing Peroxide of Chlorine:" by Messrs. F. Crace Calvert and E. Davies.
6. "On the Deposits found in the Chimneys of Gold and Silver Reverberatory Furnaces:" by Mr. J. Napier.
7. "On the Formation of Chrysammic Acid by the Action of Nitric Acid on Aporetin:" by Dr. Warren De la Rue and Dr. Hugo Müller.
8. "On the General Action of Oxidizing Agents on Sulphocyanides, and on a special reaction attending the use of Nitric Acid:" by Mr. E. A. Hadow.
9. "Mineralogical Contributions, containing Notices of Meteoric Iron from Zacatecas in Mexico; Pseudomorphous Cinnabar from Spain; Libethenite from Southern Africa; Columbite from Greenland:" by Dr. Hugo Müller.

10. "On the Production of some new Ureas:" by Dr. Hofmann.

11. "On the Analysis of the Water of a Spring at Billingborough, in Lincolnshire:" by Mr. Kynaston.

12. "On Bibromacetic Acid:" by Messrs. Perkin and Duppa.

13. "On the Analysis of the Water of Holywell, North Wales:" by Mr. James Barratt.

14. "On the Relations of the Atomic Weights of the Elements:" by Mr. J. Mercer.

15. "On the Detection of Alum in Bread:" by Mr. John Horsley.

16. "On some Minerals containing Arsenic and Sulphur from Chili:" by Mr. F. Field.

17. "On the Presence of Ammonia in Ice, and on the Action of Ice-water upon Lead:" by Dr. Medlock.

18. "On Titanic Acid:" by Mr. E. Riley.

19. "On the Conversion of Lactic Acid into Propionic Acid:" by Dr. C. Ulrich.

20. "On some Native Combinations of Oxide of Mercury and Oxide of Antimony:" by Mr. F. Field.

21. "On the Constitution of Lactic Acid:" by Professor Kolbe.

22. "On a New Method for the Quantitative Estimation of Nitric Acid:" by Dr. Pugh.

23. "On Sorbic Acid:" by Dr. Hofmann.

24. "On some Derivatives from the Olefines:" by Dr. Guthrie.

Discourses have been delivered,

"On Atoms and Equivalents:" by Dr. Odling.

"On the Air of Towns:" by Dr. R. Angus Smith.

"On Ammonia:" by Dr. Hofmann.

"On the Composition of the Animal Portion of our Food, and on its Relation to Bread:" by Dr. Gilbert.

"On the Colouring Matters of Madder:" by Dr. E. Schunck.

It will be evident from the above list that not only has chemistry been steadily progressing during the past year, but that contributions of very considerable interest have been made to this Society. The papers of Messrs. Perkin & Duppa, and of Dr. Ulrich have gone far to establish the position of the glycolic and lactic acids in their relations to the fatty acids of the primary series; while the curious results of Mr. Wanklyn, which resulted in the formation of propionic acid from the action of carbonic anhydride upon sodium-ethyl, point out a new mode of transferring compounds from one homologous group to that immediately below it. Dr. Hofmann's researches on the ammonias and ureas have undergone great elaboration, while his investigation of the distillate from the juice of the mountain-ash berry has resulted in the discovery of a new fatty acid, of great interest, both in its composition and properties.

It is unfortunate that the examination of natural organic products has of late been somewhat neglected: for by such investigations only can chemists hope to fill up the many gaps that now exist in the series of organic groups, the completion of which is essential to the comprehension of the collateral relations of organic bodies.

The departments of mineral and analytical chemistry have likewise received valuable contributions, among which may be mentioned, in particular, Dr. Pugh's ingenious process for the estimation of nitric acid.

The Council have also to congratulate the Society upon that great indication of prosperity, a good balance-sheet.

During the past year, death has removed from among us a man whose active labours in science, both in its abstract and applied fields, have gained for him a wide-spread and well-earned reputation; we allude to Hugh Lee Pattinson, who expired at his residence at Scot's House, Newcastle-upon-Tyne, on the 11th Nov., 1858.

Our lamented Fellow was born at Alston, where his parents, belonging to the smaller landholders of that locality, had for generations resided, and in which place he received such an education as its school afforded. His, however, was not one of those minds which are dependent for their development on the assistance of others. Gifted with great powers of observation, and endowed with habits of accurate thought, Mr. Pattinson, at an early period in life, gave proof of an intellect of no common order.

A subordinate appointment at a soapery in Newcastle gave him

an opportunity of pursuing his studies in chemistry, to which his attention had been directed by accidentally hearing a lecture on that science. These studies were pursued with such ardour and perseverance, that, a few years afterwards, when the Commissioners of Greenwich Hospital required an assay master for their mines in Alston Moor, Mr. Pattinson was found by the authorities to have sufficiently qualified himself by self-instruction to undertake the very responsible duties of the situation.

This new field afforded him ample scope for pursuing his favourite investigations; and among the varied subjects which engaged his attention, the process, as then carried on, for separating silver from lead occupied a prominent position. Previous to the discovery which connects his name in so distinguished a way with metallurgical science, silver was obtained from its associated lead by the conversion of the last-named metal into litharge, leaving the pure silver behind, which litharge had to be reconverted into lead, at considerable expense in each process and with considerable loss of metal. After a great number of unsuccessful attempts to effect the separation of these substances by a less circuitous method, Mr. Pattinson discovered that a mixture containing only a very few ounces of silver to the ton of lead appeared to resolve itself into two portions, one remaining fluid after the other had assumed a solid and granular condition. It occurred to him that, possibly, there might be a difference in the quantity of silver contained in these two portions. Repeated experiments established the correctness of this supposition, and its value as applied to separating the two metals was at once perfectly apparent. The process after being matured was patented, and very soon became extensively used as the *Pattinson process* of desilverizing lead. Its economy of application was such, that certain kinds of this metal, which previously would not bear the expense of having the silver extracted, could now be profitably handed over to the refiner, and this to such an extent, that it has been estimated that 54,000 ounces of silver are now annually added to our productions of this precious metal, which, previous to Mr. Pattinson's discovery, would have remained uselessly as an impurity of lead. At a later period, Mr. Pattinson added to the advantages he had conferred on applied chemistry, by his discovery of a simple means of extracting magnesia from the limestone rock containing that earth, by means of carbonic acid; and, afterwards, returning to his original field of investigating the properties of lead, he discovered a rapid method

of producing, direct from lead ore, a beautiful pigment now extensively used and known as *Pattinson's oxychloride of lead*. The manufacture of these two substances forms the chief produce of a very extensive manufactory, established by him and his partners, at Washington, in the county of Durham. His position as one of the proprietors of these works, together with being largely interested in those of a still more extensive character at Felling for the manufacture of soda, alum, bicarbonate of soda, and other substances, gained for Mr. Pattinson a very prominent place among the chemical manufacturers of this kingdom.

The scientific pursuits, however, of our deceased member were neither exclusively directed to the acquisition of wealth nor to the founding of lucrative concerns. A considerable amount of attention was bestowed on the study of electricity and the allied science of magnetism; and it was by his acute observation that the development of frictional electricity was first detected in high pressure steam when escaping from a small aperture. Subsequently, he devoted much time to the study of astronomy, and, at great expense, erected at Scot's House a very powerful telescope, equatorially mounted, an instrument which was employed by Professor Smythe in his observations on the Peak of Teneriffe.

The Royal, the Astronomical, and other learned Societies recognized the scientific attainments of Mr. Pattinson by electing him a Fellow of their respective Institutions.

Thornton John Herapath, youngest son of William Herapath, Esq., F.C.S., &c., Analytical Chemist and senior Magistrate of Bristol, was born in that city in the year 1830. His chemical education was received in his father's laboratory, and his labours commenced at a very early age. At thirteen he began analysis; his first published paper was printed when he was sixteen, and his first course of public lectures was given when he was eighteen. He worked incessantly, not only in Chemistry, but also in Microscopy, Botany, Entomology, Natural History, and Philosophy. At the age of twenty-six, he accepted the appointment of chief chemist to the Mexican and South American Smelting Company, for three years, during which time he resided at Herradura, near Coquimbo, in Chili, and in the intervals of his duties pursued his researches into the natural productions, manners, habits, &c., of the inhabitants, sending home drawings, specimens, or descriptions of everything he thought worthy of note. At the end of his engagement, he proposed visiting his native land; but on his voyage home he was

unfortunately drowned, on December 9th, 1858, at the age of twenty-eight. His person was tall and very thin; his character truthful, honest, and conscientious. Kind-hearted and generous, he was a universal favourite wherever he went. As a proof of his ardour in science, he made a long series of experiments upon the physiological effects of several poisons (phosphuretted oil, nux-vomica, &c.) upon his own system, continuing them as far as they could be endured. He was an indefatigable contributor to chemical science, having published no fewer than sixty-one papers, several of which appeared in the Journal of this Society. At the period of his death, he was engaged in the production of a series of tables of specific gravity, hardness, boiling and melting points, solubility, &c., of organic and mineral substances, together with a list of all known organic substances; the manuscript of which he has left in a state ready for publication.

The late Professor Gregory, of Edinburgh, whose death occurred on the 24th of April, 1858, was the fourth son of Dr. James Gregory, who for a period of thirty-one years discharged the duties of Professor of the Practice of Physic in the University of Edinburgh. William Gregory was born in December, 1803, and was therefore fifty-four at the time of his death. He was a graduate in medicine of the Edinburgh school, but had no hereditary fondness for the practice of the profession in which so many of his ancestors had distinguished themselves. On the contrary, at the period of his graduation, his mind was made up to follow chemistry. His brother, James Crawford, who had previously taken the Edinburgh medical degree—and who continued in practice till 1832, when he was cut off by typhus—and Duncan, who at the time of his death was a Fellow of Trinity College, Cambridge, were both distinguished for their talents and acquirements. Of William it may be averred that such was his genius that he would probably have become distinguished in any department of science he might have chosen to pursue. "His love of science," says his distinguished relative, Dr. Alison, "manifested itself at an early period. He had been present at an introductory lecture by Dr. Hope, which was illustrated by striking experiments. Several of these experiments he contrived to repeat by means of a rude apparatus which he constructed for the purpose. From that time he had always before him the object of ambition which he ultimately attained."

Soon after his graduation, Dr. Gregory went to the Continent,

and there, in the laboratories of foreign chemists, perfected his acquaintance with the practical details of his favourite science, after which he returned to Edinburgh, and commenced public life as an Extra-academical Lecturer on Chemistry. Whilst so occupied —as he was wont to relate—his chemical career was well nigh suddenly terminated by the accidental explosion of a large quantity of chloride of nitrogen in a basin. The late professor was remarkable for his coolness and self-possession under circumstances which would have been, to say the least of it, trying to many. On one occasion, during his lecture, a tube of peroxide of chlorine burst in his hand, and a fragment of glass entering his eye, caused the aqueous humour to escape—nevertheless, he proceeded with his lecture and finished it.

When Professor Graham succeeded Dr. Edward Turner in University College, London, Dr. Gregory was appointed to succeed the present Master of the Mint in the Andersonian University, Glasgow. Soon after his removal to that place, a tempting opening in Dublin induced him to go to Ireland, and commence lecturing in on one of her metropolitan medical schools. In 1839 he was appointed Professor of Medicine and Chemistry in King's College, Aberdeen, "and thus became the occupant of a chair which more than one of his distinguished ancestors had already filled." In 1844, he was elected by the patrons to succeed Dr. Hope in the Edinburgh University, in which college he continued Professor of Chemistry up to the time of his death.

In his system of chemical teaching Dr. Gregory assumed the impossibility of doing justice to the subjects—Heat, Light, Electricity and Magnetism—and though from his education, tastes, and philosophical capacity fully qualified to teach and illustrate each of these, he considered the study of the imponderables in a course of chemistry-proper an encroachment on the time, already too short in a university session, for discussing the chemistry of the ponderable elements. So fully, however, was he alive to the importance to the chemical student of a more than general knowledge of these agents, that he had devised, and would, had his health permitted, have given, a separate and complete course of lectures upon each. "He had formed plans," says his biographer already quoted, "which, had his health permitted, would have resulted in a course of chemical instruction not surpassed in extent and importance in any single school in Europe."

In his manner of teaching, Dr. Gregory was simple, precise,

and accurate. By means of a memory singularly retentive, he could at any moment cover the boards of his lecture-room with the most complicated organic formulæ. Having early in life attached himself as a working chemist to the organic department of the science, it was not surprising that as a lecturer he should principally delight in the delivery of the organic portion of his course. His organic lectures were his favourites, and so efficiently was he prepared by past experimental experience, and by daily reading, for the enunciation of even the latest discoveries, that, when lecturing on Organic Chemistry, he did not employ even the scanty notes which it was his habit to make use of when lecturing on inorganic subjects.

As a teacher, he was simple and earnest, exhibiting at all times that calm dignity and gentlemanly bearing which gave weight to his prelections and impressed his students with confidence and respect.

"As a scientific man," Dr. Balfour has rightly remarked in a biographical sketch of his former colleague, read to the Botanical Society of Edinburgh, "Dr. William Gregory worked more for utility as a teacher than for fame as a discoverer." Amongst his published papers may be noticed, Investigation of Fat from a Putrid Animal Subject; Preparation of Hippuric Acid; Preparation of Creatine; On the Presence of Nickel and Cobalt in Commercial Oxide of Manganese; Purification of Chloroform; Application of Acetate of Lead in Sugar-refinery; On the Ammoniacal Compounds of Cobalt; On a Peculiar Benzoate of Potash; On Pyroxanthine; On the Decomposition Products of Uric Acid; On the Spontaneous Decomposition of Alloxan; On a New Magnesian Phosphate. Besides these and many more investigations of the same kind, Dr. Gregory contributed to practical science improved processes for the preparation of hydrochloric acid, muriate of morphia, and oxide of silver.

The complete knowledge which he possessed of all that had been done in chemistry, up to the contents of the very last Journal; his familiar acquaintance with the modern languages; and his talent for collecting and condensing what was really of scientific importance: made him invaluable as a writer. He, moreover, wrote with ease, and could, even under the pressure of other business, write off pages of manuscript composition, for which few corrections were afterwards required. His class text-book was his "Outlines"—a work which has gone through several editions, and which, whilst it contains an extraordinary amount of informa-

tion in a comparatively small space, is remarkable for the simplicity of its arrangement, and the clearness with which its statements are expressed. From an early period of life, he attached himself to Liebig; their scientific relations were soon strengthened by personal friendship, and their affectionate intercourse continued unabated till the last. Dr. Gregory assisted Liebig in several of his courses of experiments, and some of his most important publications, he, at the request of his friend, translated and edited in this country.

"It was," says Dr. Alison, "unfortunate for Dr. Gregory that, though a man of large make, and capable during youth of much exertion, both bodily and mental, he had neither opportunity nor disposition to take so much muscular exercise as would probably have suited his physical constitution. In consequence also of an attack of fever in 1826, he became liable, during the remainder of his life, to severe pain and swelling in one of his legs, on any unusual exertion."

Owing to the state of his health latterly, he found it absolutely necessary to confine himself to such scientific investigations as required neither standing, nor walking from place to place. This species of research, the microscope afforded him the means of pursuing, and in it he engaged with all the enthusiasm of his ardent nature. Aided by his accomplished friend, Dr. Greville, Professor Gregory enriched the Transactions of the Royal Society of Edinburgh with a beautifully illustrated and laborious memoir on the Diatomaceæ. He was in constant correspondence with microscopists in every part of the world.

As a friend, Dr. Gregory was sincerity itself. His unselfish nature was opposed to the acquisition of any personal advantage which would inconvenience another, and many a circumstance attributed by others to indolence on his part was really caused by the generosity of his nature. Few applied to him for relief and went empty away. Of course, his generosity was in certain cases abused.

After a painful illness of considerable duration, he died of a somewhat complicated disorder, leaving behind him to practical science, his discoveries; to its literature, his writings; and to his friends—and they are many—the memory of a man whose professional accomplishments were rendered more valuable by the modest graces of his private character.

Drs. THE TREASURER IN ACCOUNT WITH THE CHEMICAL SOCIETY OF LONDON. **Crs.**

1858.		£	s.	d.
April 1.	To Cash in hand	402	12	4½
June 22.	„ Rent from Ethnological Society to March, 1857	20	0	0
July 21.	„ Half-yearly Dividend on £150 Three per cent. Consols	2	5	0
1859.				
Jan. 22.	„ Removal Fund	50	0	0
Feb. 4.	„ Dividend on £150 Three per cent. Consols	2	5	0
March 25.	„ Sundry Receipts from 1st April, 1858, to 25th March, 1859, as below :—			
	Life Compositions £190			
	Admission Fees 72			
	„ Subscriptions due previous to 1858 :—			
	Resident Members 39			
	Non-resident do. 24			
	„ Subscriptions for 1858 :—			
	Resident Members 64			
	Non-resident do. 67			
	„ Subscriptions for 1859 :—			
	Resident Members 188			
	Non-resident do. 60	704	0	0
	£	1181	2	4½

1859.		£	s.	d.
March 25.	By General Printing	15	19	1
„ „	Editor of Journal's Salary £50			
„ „	„ „ Honorarium 10	60	0	0
„ „	„ Printing Journal	166	1	0
„ „	„ Librarian's Salary	15	0	0
„ „	„ Proceedings of Royal Society	20	0	0
„ „	„ Magazines	2	19	0
„ „	„ Subscription to Cavendish Society	1	1	0
„ „	„ T. Hux, Attendance & Cleaning to March, 1858	15	0	0
„ „	„ „ „ „ to March, 1859	20	0	0
„ „	„ „ Petty Expenses (as per Book)	4	19	9½
„ „	„ Gate Porter	1	1	0
„ „	„ Tea Expenses	11	10	9
„ „	„ Stamps, Stationery, and Postages	4	16	5
„ „	„ Collector's Commission	34	3	0
„ „	„ Clerk	2	0	0
„ „	„ Iron Safe	37	19	6
„ „	„ Furniture	57	16	6
		£ s. d.	470	7 0½
Feb. 4.	„ Purchase of £100, 3 per cent. Consols 95 2 6			
March 11.	„ „ „ „ „ 96 7 6		191	10 0
	By Balance :—			
„ 25	At Coutts and Co. 502 13 7			
„ „	Cash 16 11 9		519	5 4
	£		1181	2 4½

Assets.	£	s.	d.
Exclusive of Library, Museum, and Furniture.			
Balance in Cash	519	5	4
Invested in 3 per Cent. Consols	350	0	0
	£869	5	4

Examined and found correct,

E. W. BRAYLEY,
PHILIP J. CHABOT, M.A.,
GEORGE C. FOSTER. } *Auditors.*

London, 29th March, 1859.

XIX.—*On the Action of Boracic Acid upon the Carbonates of the Alkalies and Alkaline Earths.*

By Charles L. Bloxam.

Being engaged in the search after a direct method of valuing commercial samples of crystallized boracic acid, I made several experiments in order to ascertain whether the amount of that acid could be inferred from the weight of carbonic acid which the sample was capable of expelling from carbonate of soda.

Finding that boracic acid always expelled, at a high temperature, more than a single equivalent of carbonic acid, and that the numbers obtained were not concordant, I abandoned this method of estimating the boracic acid.

My attention was recalled to this subject by the "Researches on Silica" of Colonel Philip Yorke,* in which the author has shown that silicic acid is capable of expelling a greater weight of carbonic acid from carbonate of soda than from carbonate of potassa, and still more from carbonate of lithia. Colonel Yorke also stated, that boracic acid (in the form of borax) afforded results analogous to those given by silicic acid, but that the numbers obtained did not accord well together.

I then resumed the examination of the action of boracic acid upon the carbonates of the alkalies and alkaline earths; and since a paper read very recently at one of the Society's meetings has awakened an interest in the subject, I beg to lay my results before the Society in the hope of receiving some suggestion which may help to explain them, and may afford me some guidance in continuing the inquiry.

Action of Boracic Acid upon the Alkaline Carbonates at 212° F.

In these experiments, crystallized boracic acid was employed, which had been precipitated from solution of borax by hydrochloric acid, purified by several crystallizations, and dried in vacuo over sulphuric acid.

The carbonate of potassa was employed in the fused state, and the carbonate of soda sometimes in powder, sometimes in fused fragments.

* Phil. Trans. 1857, p. 533.

Invested in 3 per Cent. Consols 350 0 0
£869 5 4
GEORGE C. FOSTER.
London, 29th March, 1859.

The boracic acid and the alkaline carbonate were dissolved in a few drachms of water, in a platinum dish, the solution evaporated to dryness in the water-bath, and the residue dried in the water-oven till its weight ceased to vary appreciably. It was then dissolved in water, and the residual carbonic acid determined by the method of Fresenius and Will.

The results are contained in the following tables, in which the equivalent of anhydrous boracic acid (BO_3) is taken as = 34·9, the equivalent of carbonic acid as = 22, of potassa = 47, of soda = 31, of lithia = 14·5.

Action of Boracic Acid on Carbonate of Potassa at 212°.

One equivalent (34·9) of boracic acid taken in each case.

No.	Carbonate of potassa in equivalents.	Carbonic acid expelled in equivalents.
1	0·33	0·33
2	0·56	0·39
3	0·84	0·39
4	1·93	0·31
5	1·98	0·29
6	2·90	0·14

It hence appears that when three equivalents of boracic acid were employed to decompose one equivalent of carbonate of potassa, the whole of the carbonic acid was expelled at 212° F.; that when the carbonate was increased, a somewhat larger proportion of carbonic acid was expelled until the carbonate amounted to nearly one equivalent. When nearly two equivalents of carbonate of potassa were employed, rather less carbonic acid was expelled than when only one-third of an equivalent had been taken, and when nearly three equivalents of carbonate of potassa were employed for one equivalent of boracic acid, not half as much carbonic acid was expelled.

The smaller quantity of carbonic acid expelled in experiments 4, 5, and 6, might of course be accounted for by the retention of carbonic acid in combination with the excess of carbonate of potassa, but on endeavouring to make a correction for this, I found that the quantities of carbonic acid and water retained by

a given weight of carbonate of potassa at 212° F. were far from constant.*

It was not possible, therefore, to assign a formula to any of the residues, save that of experiment 1, which would be represented as $KO.3BO_3$ with 4·3 eqs. of water.†

Action of Boracic Acid on Carbonate of Soda at 212°.

One equivalent (34·9) of boracic acid taken in each case.

No.	Carbonate of soda in equivalents.	Carbonic acid expelled in equivalents.
7	0·33	0·33
8	0·51	0·42
9	1·17	0·43
10	1·24	0·52
11	1·44	0·55
12	3·53	0·66

These results are directly opposite to those obtained with carbonate of potassa, for the quantity of carbonic acid expelled increases progressively, though not nearly in the same ratio, with the quantity of carbonate of soda employed.

Here also, however, we find that the whole of the carbonic acid is expelled when three equivalents of boracic acid are allowed to act upon one equivalent of carbonate of soda.

* Three experiments were made in which weighed quantities of fused carbonate of potassa were dissolved in water, the solution thoroughly saturated with carbonic acid, evaporated to dryness on the water-bath, and dried in the water-oven till the weight was nearly constant; the mass was then dissolved in water, and the carbonic acid determined by Fresenius and Will's process. The composition of the residue was—

	I.	II.	III.
Potassa	1 eq.	1 eq.	1 eq.
Carbonic acid	1·35 eq.	1·18 eq.	1·18 eq.
Water	1·01 eq.	1·10 eq.	1·24 eq.

On dissolving 21·16 grns. of fused carbonate of soda in water, and treating it in exactly the same way, 21·10 grns. of the carbonate were obtained, showing that in this case no carbonic acid and water had been retained.

† A crystallized terborate of potassa was obtained by Laurent, containing 8 eqs. of water.

Having proved by direct experiment that carbonate of soda was not capable of retaining any excess of carbonic acid at 212° F., I was enabled to calculate the composition of the borates of soda formed in these experiments, and found that, except in experiment 11, a definite formula might be assigned to them; thus:—

No. 7	gave	2	$(NaO.3BO_3)$ + 7HO.
8	„	3	$NaO.7BO_3$ + 9HO.
9	„	3	$NaO.7BO_3$ + 6HO.
10	„		$NaO.2BO_3$ + 4·3HO.
12	„	2	$NaO.3BO_3$ + 6·6HO.

Action of Boracic Acid upon the Alkaline Carbonates at a dull red heat.

In these experiments, the materials were heated in platinum crucibles over the flame of an ordinary argand gas-burner, furnished with a copper chimney, about six inches high, and supplied with as much gas as it could burn without smoking.

The boracic acid was employed sometimes in the crystallized state, sometimes after having been dried in the water-oven.*

The alkaline carbonates were powdered and mixed with the boracic acid in the crucible. The mixtures were weighed at considerable intervals until their weight had ceased to vary more than a few hundredths of a grain. The carbonic acid expelled was ascertained by deducting the calculated amount of water from the total loss of weight.

No concordant numbers were obtained by decomposing carbonate of potassa with boracic acid at a dull red heat; but it was proved that less than one equivalent of carbonic acid was expelled by an equivalent of boracic acid, even when a large excess of carbonate of potassa was employed.

* Finding that the formula of boracic acid dried at 212° was given by Gmelin, upon the authority of Berzelius, as $3HO.2BO_3$, I dried 30·95 grns. of the pure crystallized acid in the water-oven till its weight was constant (which required about twelve hours), when it had lost 9·17 grns., or 29·62 per cent.

The formula $HO.BO_3$ would require a loss of 29·08 per cent., which is sufficiently near to the experimental result, the difference being due to the slight volatilization of the acid.

The above formula of Berzelius would require a loss of only 21·8 per cent. It will be seen that several of the experiments detailed in this paper confirm the formula $HO.BO_3$ for boracic acid dried at 212°.

Action of Boracic Acid upon Carbonate of Soda at a dull red heat.

One equivalent (34·9) of boracic acid taken in each case.

No.	Carbonate of soda in equivalents.	Carbonic acid expelled in equivalents.
13	1·24	1·02 ($3HO.BO_3$)
14	1·24	1·03 ($HO.BO_3$)
15	1·24	1·07 ($3HO.BO_3$)
16	1·24	1.02 „
17	1·50	1·00 „
18	2·20	1·01 ($HO.BO_3$)
19	2·90	1·00 ($3HO.BO_3$)
20	3·10	1·05 „
21	3·10	1·02 „
22	3·10	0·99 „
23	3·10	1·01 „
24	3·10	1·00 „

Mean of 12 experiments 1·018

In these cases the mixture had never fairly fused, but had merely fritted together.

At a dull red heat then, hydrated boracic acid expels one equivalent of carbonic acid from carbonate of soda, and it cannot fail to be remarked that this result is uniformly obtained, notwithstanding the great variation in the proportion of carbonate of soda employed.

It appeared probable that the amount of boracic acid contained in a commercial sample might be inferred from the quantity of carbonic acid expelled from carbonate of soda at a dull red heat; but it was found that the boracic acid then displaced more than a single equivalent of carbonic acid, the escape of the latter being facilitated by the presence of ammoniacal salts in the crude boracic acid.

Action of Boracic Acid upon Carbonate of Lithia at a dull red heat.

One equivalent (34·9) of boracic acid taken in each case.

No.	Carbonate of lithia in equivalents.	Carbonic acid expelled in equivalents.
25	3·47	2·53
26	3·07	2·42

The boracic acid and the carbonate of lithia were both employed in the fused state. Anhydrous boracic acid is able to expel $2\frac{1}{2}$ eqs. of carbonic acid from carbonate of lithia at a dull red heat.

Action of Boracic Acid upon the Alkaline Carbonates at a bright red heat.

The materials were fused in platinum crucibles over a Solly's gas-furnace, for ten or fifteen minutes, then weighed, and again ignited for five or ten minutes until the weight did not vary in any considerable degree.

A few preliminary experiments were made to ascertain the effect of this temperature upon the separate re-agents; and since this has of necessity a very important bearing upon the results, it may be desirable to refer to the experiments upon boracic acid, since some doubt might be entertained of its resistance to so high a temperature.

30·95 grns. ($\frac{1}{2}$ eq.) of crystallized boracic acid were heated to dull redness over an argand gas flame, when they lost 14·13 grns., of which only 13·5 grns. would be water, the remaining 0·63 representing the volatilized boracic acid (3·61 per cent. of the dry acid employed).

16·82 grns. of vitrefied boracic acid thus obtained were heated for ten minutes in a loosely covered platinum crucible over the gas furnace, when they had lost 0·21 grn. (1·24 per cent.)

When again heated for ten minutes in the open crucible, bubbles were seen to form within the mass, and a further loss of 0·29 grn. was perceived.

5·99 grns. of well vitrefied boracic acid taken from the stock employed for the following experiments, were very strongly ignited over the gas-furnace, in a covered crucible, for five minutes, when the loss amounted to 0·14 grn., or 2·33 per cent. When again

heated for five minutes, it suffered no further diminution; ignited a third time for seven minutes, it had not lost, though a fourth ignition for five minutes caused a loss of 0·02 grn.

On igniting for five minutes in the open crucible, the loss was 0·02 grn., and in the next five minutes 0·04 grn.

These numbers lead to the inference that even supposing the boracic acid to be volatilized to the same extent in the presence of an excess of an alkaline carbonate, the results will be but slightly vitiated; for, taking the whole loss in twenty minutes' ignition, in the first experiment, it would represent only $\frac{1}{212}$ of an equivalent of carbonic acid for each equivalent of boracic acid.

I also convinced myself that neither carbonate of potassa nor carbonate of soda suffered any material diminution of weight at this temperature.

The behaviour of carbonate of lithia was very different.

The carbonate of lithia employed was carefully tested for all impurities except potassa and soda, the absence of any material quantities of these being inferred from the circumstance that 5 grns. of the carbonate, when decomposed by sulphuric acid, gave 7·34 grns. of sulphate of lithia, representing 4·91 grns. of the carbonate.

The carbonate of lithia was dried in an air-bath at about 300° F. until its weight was constant.

12·74 grns. of the carbonate were strongly ignited over the gas furnace in a covered platinum crucible, until the weight did not vary more than 0·09 grn.

The loss amounted to 8·38 per cent.

12·66 grns. of the carbonate lost 1·05, or 8·29 per cent.

13·54 grns. lost 1·14 or 8·41 per cent.

5·53 grns. of carbonate of lithia, ignited till its weight did not vary more than 0·01 grn. after five minutes' ignition, had lost 0·83 or 15·0 per cent.

The ignited mass, treated with sulphuric acid, gave 7·94 grns. of sulphate, which would correspond to 5·317 grns. of carbonate of lithia, or 0·213 grn. less than was originally taken, and 0·617 grn. more than if the mass after ignition were pure carbonate of lithia.

The ignited mass must therefore have contained uncombined lithia, the carbonic acid having been partially expelled.

The loss of lithia would be accounted for by its volatilization during the repeated ignition.

13·14 grns. of carbonate of lithia lost 1·53 or 11·6 per cent.

13·2 grns. lost, when ignited till it absolutely ceased to diminish after five minutes ignition, had lost 1·34, or 10·15 per cent.

1·58 grns. of carbonate of lithia, ignited till the variation did not exceed 0·01, had lost 10·70 per cent. It was dissolved in water, and decomposed by an excess of chloride of barium; the liquid filtered from the carbonate of baryta was strongly alkaline, both to litmus and turmeric, indicating the presence of lithia in an uncombined state.

On treating the original carbonate of lithia in the same way, the filtrate was very feebly alkaline to litmus, and not at all to turmeric.

From these experiments it is evident that the carbonate of lithia is partially decomposed by a bright red heat, but that only a fraction of the carbonic acid can be thus expelled, a limit being reached in every experiment, at which the retaining power of the lithia was in equilibrium, for that temperature, with the tendency of the heat to expel the carbonic acid.

The maximum amount of loss, it will be observed, was 15 per cent., which occurred in ignition for twenty-five minutes. This is only one fourth of the total amount of carbonic acid (60·02 per cent.) which the carbonate of lithia contains.

To diminish, as far as possible, the errors arising from this decomposition of carbonate of lithia, the carbonate used in the following experiments was always ignited, at the temperature of the experiment, until its weight ceased to vary materially in periods of five minutes, before adding the boracic acid.

Action of Boracic Acid upon Carbonate of Potassa at a bright red heat.

One equivalent (34·9) of boracic acid taken in each case.

No.	Carbonate of potassa in equivalents.	Carbonic acid expelled in equivalents.
27	1·23	1·08
28	1·27	1·08
29	1·60	1·11
30	1·63	1·12
31	1·73	1·15
32	1·73	1·22
33	1·75	1·14
34	1·77	1·18
35	1·83	1·14
36	2·44	1·24
37	2·75	1·20
38	2·77	1·24
39	2·81	1·23
40	3·18	1·21
41	3·53	1·23
42	3·64	1·26
	Mean of 16 experiments	1·17

The boracic acid and the carbonate of potassa were both employed in the fused state.

An examination of this table shows that, at a bright red heat, boracic acid expels somewhat more than one equivalent of carbonic acid from the carbonate of potassa, and that the amount of carbonic acid expelled usually increases with the proportion of alkaline carbonate taken, though to a comparatively slight extent, the minimum being 1·08 eqs. of carbonic acid, when 1·25 eqs. of carbonate of potassa were employed, and the maximum 1·26 eqs. of carbonic acid for 3·64 eqs. of carbonate of potassa.

It was not difficult to obtain a nearly constant weight in these cases, one or two weighings being generally found to suffice if the mass was heated at first for about fifteen minutes, and, after weighing, for periods of five minutes.

The fused masses, when cool, appeared to be composed of delicate prismatic crystals of a fine blue colour, for which I was unable to assign a cause.

Action of Boracic Acid upon Carbonate of Soda at a bright red heat.

One equivalent (34·9) of boracic acid taken in each case.

No.	Carbonate of soda in equivalents.	Carbonic acid expelled in equivalents.	
43	1·50	1·48	$(3HO.BO_3)$*
44	2·01	1·88	$(HO.BO_3)$
45	2·02	1·81	„
46	2·20	1·95	„
47	2·28	1·88	(BO_3)
48	2·90	1·89	$(3HO.BO_3)$
49	3·10	1·73	„
50	3·10	2·04	„
51	3·10	1·93	„
52	3·39	2·22	(BO_3)
53	4·40	1·85	$(HO.BO_3)$
54	5·41	2·34	(BO_3)
55	5·44	2·52	„
56	5·58	2·31	„

The experiments numbered 44, 46, 49, 50, 51, 52, and 53 were made in a muffle, the rest over the gas-furnace.

* The borate here formed would have the composition $3\ NaO.2BO_3$; and, according to Gmelin, this salt was obtained by Arfvedson in the fusion of borax with carbonate of soda, when each atom of borax expelled two atoms of carbonic acid. Three experiments, which I made by fusing borax with excess of carbonate of soda in a hot muffle, agreed very nearly with the supposition that three atoms of carbonic acid were expelled by each atom of borax, thus producing a borate of the formula $2NaO.BO_3$. It will be seen that this accords with the general result of the experiments made with free boracic acid, viz. that each atom of the acid may expel two atoms of carbonic acid, thus combining with two atoms of soda. In some analyses of samples of commercial boracic acid by this method, in which forty-four parts of carbonic acid expelled from the carbonate of soda were taken to represent 34·9 parts of BO_3, the percentage of boracic acid agreed very closely with that obtained by determining all the other constituents of the samples separately, but the circumstance that a large proportion of carbonic acid may be expelled by samples containing a small percentage of boracic acid, in consequence of the increase in the proportion borne by the carbonate of soda to the acid, renders this method too uncertain, except in cases were the percentage of boracic acid is already approximately known.

In the experiments numbered 46, 49, and 52, the residual carbonic acid was determined and found to confirm the result inferred from the loss of weight, proving that no appreciable volatilisation of boracic acid had taken place.

The fused masses were greyish white, never blue, as in the cases where carbonate of potassa had been employed.

The difficulty of obtaining a constant weight in these experiments was very remarkable, as many as eight or ten weighings being often found necessary.

It will be noticed that the increase of the amount of carbonic acid expelled according to the proportion of carbonate of soda employed, is very much more marked than in the case of carbonate of potassa, the mininum being 1·48 eqs. of carbonic acid expelled from 1·50 eqs. of carbonate of soda, and the maximum 2·52 eqs. of carbonic acid from 5·44 eqs. of carbonate of soda.

The amount of carbonic acid expelled by boracic acid from carbonate of soda at a bright red heat, may therefore be said to range between $1\frac{1}{2}$ and $2\frac{1}{2}$ eqs., though in the majority of the above experiments it approached more nearly to 2 eqs. than to either of these limits.

The masses obtained in these fusions were always very deliquescent, and far more caustic to the taste and touch than carbonate of soda.

Action of Boracic Acid upon Carbonate of Lithia at a bright red heat.

One equivalent (34·9) of boracic acid taken in each case.

No.	Carbonate of Lithia in equivalents.	Carbonic acid expelled in equivalents.
57	2·98	2·47
58	3·07	2·66
59	3·47	2·70
60	3·50	2·53
61	5·10	2·45
Mean of 5 experiments		2·56

The results with carbonate of lithia are seen to be nearly as constant as those with carbonate of potassa, and it was even

easier to obtain a constant weight in the case of carbonate of lithia.

It appears then, that, at a bright red heat, boracic acid is able to expel $2\frac{1}{2}$ eqs. of carbonic acid from carbonate of lithia, a result which agrees with that obtained at a dull red heat.

Action of Boracic Acid upon the Carbonates of Baryta and Strontia.

Pure precipitated carbonate of baryta is not materially affected by the heat of the gas-furnace, as the following experiments prove:—

14·84 grns. of carbonate of baryta, ignited in a covered crucible for ten minues, had lost only 0·04 gr.

14·42 grns., ignited very strongly for fifteen minutes, had lost only 0·11 grn.

Carbonate of strontia is, as would be expected, decomposed to a greater extent.

15·88 grns., heated for five minutes over the gas-furnace, had lost 0·25 grn.; on heating again for five minutes, it lost 0·02 grn. Total loss, 1·7 per cent.

11·84 grns. lost, in four successive periods of five minutes, 0·15, 0·10, 0·18, and 0·17 grn. Total loss, 5·07 per cent.

12·43 grns. lost, in three successive periods of five minutes, 0·29, 0·16, and 0·05 grn. Total loss, 4·34 per cent.

It will be seen, however, that the decomposition of carbonate of strontia by heat will not materially affect the general result of the experiments, for taking even the greatest amount of loss in the above experiments, it would represent only 3·74 of carbonic acid (about $\frac{1}{6}$ eq.) lost by one equivalent (73·8) of carbonate of strontia.